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# EXISTING NEEDS IN THE EXPERIMENTAL AND OBSERVATIONAL STUDY OF ATMOSPHERIC CHEMICAL REACTIONS

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16. Abstracts This report contains recommendations to aid those concerned with photochemical modeling in planning studies. The suggested programs are designed to provide information needed to develop kinetic models to describe the chemical transformations of atmospheric pollutants. The core of this report focuses on kinetic and mechanistic studies of individual reactions, smog chamber studies, and atmospheric measurement programs that the authors feel should be undertaken to provide the necessary data for model development. Existing deficiencies in knowledge in each of these areas are discussed and the types of programs needed to provide the missing information are examined in detail. The report also includes a short history of model development, describing the various photochemical mechanisms developed to date.

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## I. INTRODUCTION

A great many experimental and observational programs have been carried out over the years in an effort to increase our knowledge of atmospheric chemical reactions. Carefully conceived laboratory experiments have provided the basis for estimation of individual rate constants. Smog chambers studies have served as an important aid in establishing a qualitative understanding of the overall smog formation process. Atmospheric observations have also proven valuable in this respect, and in addition, in the identification of pollutant species. Within the last four years, however, advances in the development of mathematical descriptions of the photochemical reaction process have created a need for refined experimental and observational programs, programs geared to yielding information either of much greater accuracy than seemed necessary five or ten years ago or of a type or kind that has rarely been collected in the past.

Two major "breakthroughs" have spurred the interest in increasingly complex and sophisticated experimentation in the field of atmospheric chemistry--

> the development of photochemical kinetics mechanisms capable of describing the concentration-time behavior of the major reactants and products, as monitored in a smog chamber. While the comparisons between prediction and observation have often been good for experiments having a variety of initial conditions, the hydrocarbon reactant has generally been a single species or binary mixture.

the development of mathematical models capable of predicting the concentrations of photochemical pollutants as a function of location and time over a region of the order of two to five thousand square miles (i.e., a major metropolitan airshed). The spatial resolution of such models is typically of the order of one to two miles.

While development of both types of models has proceeded rather smoothly and swiftly over the past three years, it became apparent at an early stage that *there presently exists no data base of sufficient accuracy and detail to properly support model validation studies.* A major purpose of this report is to specify in general terms experimental and observational programs that will meet this need.

But the collection of data for model validation purposes alone suggests a rather narrow horizon. We see as a primary value of model development the codification of knowledge in the field of study, the "pulling together" of the many bits and pieces in an attempt to gain an expanded understanding of the whole. When viewed in this way, the mounting of an experimental program with a model, models, or modeling as the structural foundation for the pursuit is a major step forward--from gaining knowledge in a piecemeal fashion (and understanding often with long delays) to gaining knowledge efficiently, in quantity, and in a coordinated manner.* It is the purpose of this report to discuss future needs in the measurement and observation of atmospheric reaction processes with the broader perspective--with the unifying element of the mathematical model, our best descriptor of the dynamic processes that we are attempting to understand.

---

* The notion of *coordinating* all elements of an experimental and observational program is of great importance. For example, if the concentration-time predictions of a validated kinetic mechanism are relatively insensitive to the magnitude of a particular rate constant, there is little point in expending effort to improve the accuracy of its estimated value. Science is better served by concentrating efforts in areas in which an increase in knowledge pays a greater reward. The model serves admirably as a tool for identifying such efforts.

If we are to deal with the subject of atmospheric reactions in a unified manner, it is necessary to discuss mathematical modeling at an early stage. In Chapter II, we examine the nature of the photochemical mechanism (i.e., its mathematical structure, the degree of detail it incorporates, etc.) and present a short history of model development. We then discuss the need for lumping of hydrocarbon and radical species and suggest a mechanism (not yet subjected to verification) that has strong potential for accurately describing the concentration-time behavior of all measurable species (except, of course, those that are lumped). Model assumptions are carefully stated and the validation procedure is described. Finally, we outline the alterations that must be made in any kinetic mechanism if it is to be incorporated into an urban airshed model.

In Chapter III, we present a full discussion of the two major classes of urban airshed models--the Eulerian and the Lagrangian. Fundamental equations are presented and applied forms of the equations are derived so that the assumptions on which the latter are based can be clearly discerned. The two commonly applied types of models--the grid and the trajectory--are detailed, and their advantages and shortcomings are discussed. Levels of uncertainty associated with input variables to these models--emissions and meteorological--are presented. The chapter concludes with a section summarizing possible avenues of pursuit for improving the present generation of models.

The remaining three chapters, IV, V, and VI, are, in many ways, the core of the report. They deal, respectively, with laboratory studies concerned with the kinetics and mechanisms of individual reactions, smog chamber studies, and atmospheric observations. In each, we discuss existing deficiencies in knowledge, examine in detail the types of studies needed, and recommend specific studies and/or general programs. Thus, the three chapters, taken as a whole, constitute a comprehensive review, analysis, and diagnosis of needs in experimentation and observation of the atmospheric chemistry of contaminants.

## II. KINETIC MECHANISMS FOR ATMOSPHERIC PHOTOCHEMICAL REACTIONS

The formulation of a kinetic mechanism of general validity for atmospheric photochemical reactions is an endeavor beset by several inherent difficulties:

(1) There is a multiplicity of stable chemical species present in the atmosphere. Most of these exist at very low concentrations, thereby resulting in major problems in detection and analysis. A number, in fact, probably remain unidentified.

(2) There is a large variety of unstable species (highly reactive, short-lived intermediates) in the atmosphere. These species cannot be measured because of their extremely low concentrations and high reactivities.

(3) Among the stable and unstable species, there are literally hundreds of potential chemical reactions that may be occurring.

However, while we must admit to only a limited knowledge of atmospheric reaction processes, it remains essential that we attempt to formulate quantitative descriptions of these processes which are suitable for inclusion in an overall simulation model. The general considerations of, the progress toward, and the remaining problems in the development and validation of a generalized mechanism for atmospheric photochemical reactions that is to be included in an overall airshed model are the subjects of this chapter.

### A. The Nature of the Photochemical Smog System

The general features of the concentration-time behavior of the photochemical smog system are shown in Figure 1. These data were obtained by Altshuller et al. (1967). Although the experimental data in Figure 1 involve only the single hydrocarbon propylene, propylene photoxidation in the presence of $NO_x$ manifests the major characteristics of photochemical smog. The rate of decrease of both propylene and NO does not reach a substantial value immediately after the lights are turned on, suggesting an induction period. After the apparent induction period NO is rapidly oxidized to $NO_2$. The concentration of NO reaches a low value which persists throughout the latter stages of the reaction. At about the time the $NO_2$ concentration reaches a maximum, measurable $O_3$ formation begins to take place. The subsequent loss of $NO_2$ is attributable to formation of organic pernitrates and nitric acid. Additional stable organic products such as formaldehyde (HCHO) and acetaldehyde ($CH_3CHO$) also form in the propylene-$NO_x$ system.

It has been observed that the peak amount of $O_3$ produced over a fixed time of irradiation increases rapidly, goes through a maximum, and finally decreases as one performs a series of controlled experiments in which the initial hydrocarbon concentration is held constant and the total initial concentration of $NO_x$ is increased. We illustrate this phenomenon qualitatively in Figure 2.

Although the data shown in Figure 1 are indicative of the concentration behavior in atmospheric photochemical smog, a number of factors may serve to make the chemical behavior in a smog chamber differ from actual atmospheric chemistry:

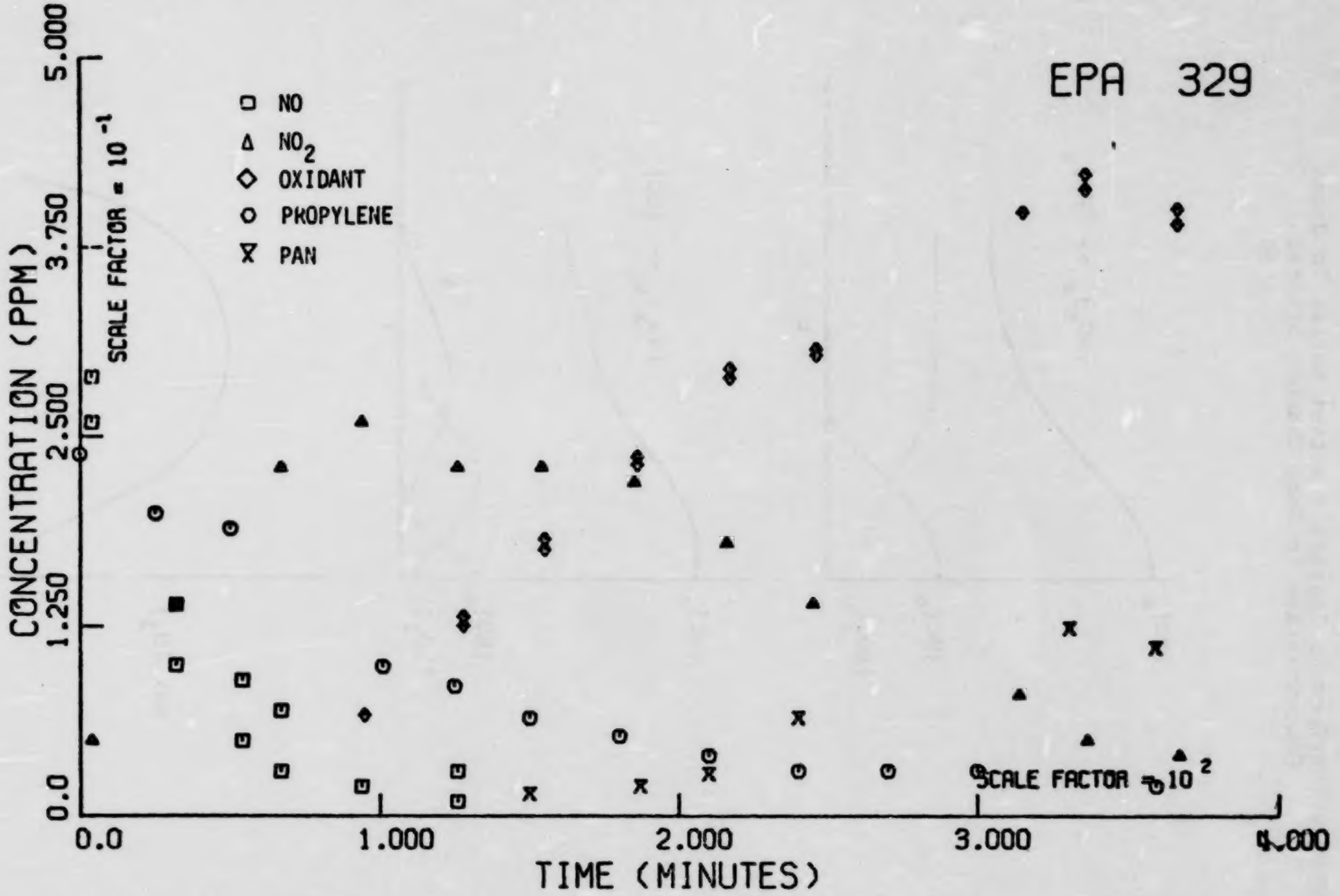
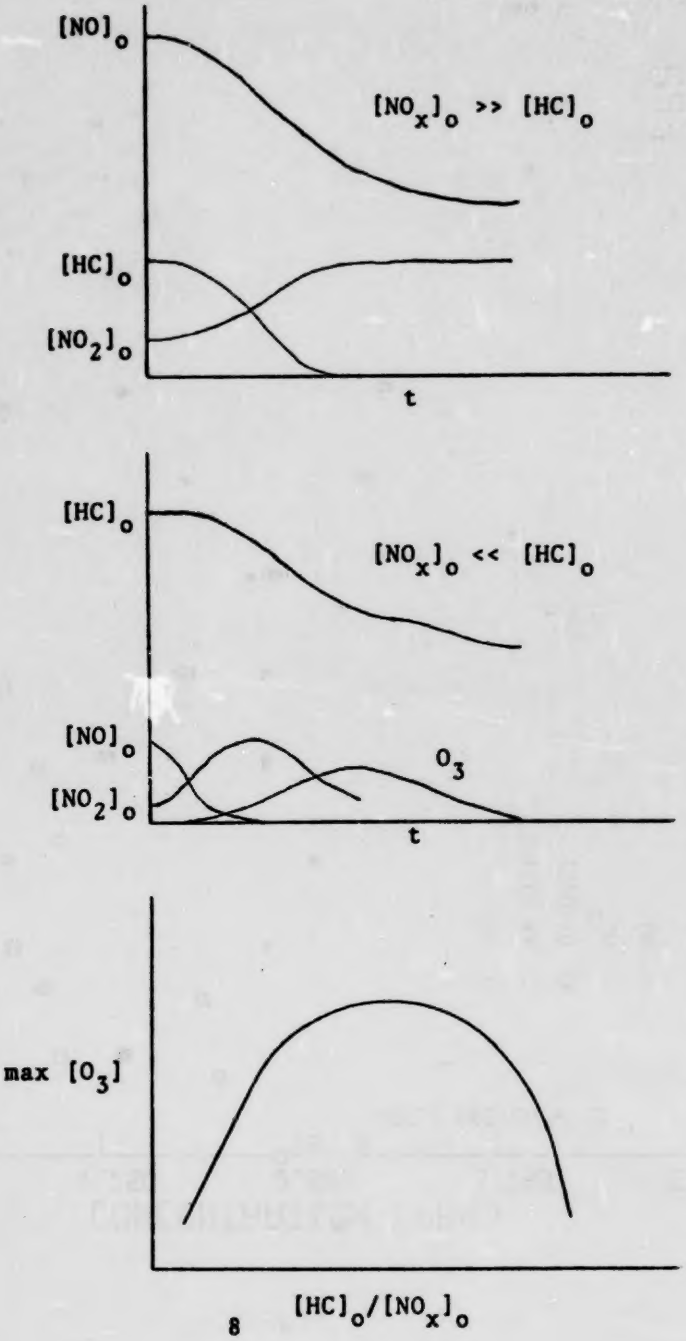


FIGURE 1. Concentration-Time Behavior of Photochemical Reactants and Products in Smog Chamber

FIGURE 2. Effect of Initial Reactant Ratios On Ozone Concentration in Smog Chamber Studies



(1) Wall effects which may be present in a chamber cannot at this time be related to ground level surface effects in the atmosphere,

(2) Most smog chamber experiments reported to date have not included oxides of sulfur or aerosols in the initial mixture. In most cases, these two classes of species are present in the atmosphere,

(3) Concentration levels employed in smog chamber experiments are often higher than atmospheric levels, and

(4) The intensity and distribution of artificial radiation employed in a chamber may not be representative of solar radiation.

In spite of these potential problems, smog chamber studies are a necessity in understanding the chemistry of the smog system. This is so because it is virtually impossible to isolate chemical reaction effects from those of transport and diffusion in the atmosphere.

### B. The Nature of Photochemical Kinetic Mechanisms

The object of developing a kinetic mechanism for photochemical smog is to enable the prediction of both smog chamber reaction phenomena, such as is illustrated in Figures 1 and 2, and atmospheric reaction phenomena. There are some general considerations which are important in developing such a mechanism. First, the mathematical description of the mechanism (in terms of the number of species included) must not be overly complex, as computation times for the overall airshed model within which the mechanism is to be imbedded are likely to be excessive. On the other hand, an overly simplified mechanism may omit important reaction steps, and thus be inadequate to describe atmospheric reactions over a range of conditions. A major requirement, then, is that the mechanism predict the chemical behavior of a complex mixture of many hydrocarbons, yet that it include only a limited degree of detail. Thus, the mechanism must strike a careful balance between compactness of form and accuracy of prediction.

A kinetic mechanism, once developed, must be validated. This procedure is commonly conceived as consisting of two parts: validation in the absence of transport processes and validation in their presence. In practical terms we are speaking, respectively, of comparison of the model's predictions with data collected in smog chamber experiments and with data collected at contaminant monitoring stations in an airshed. When we speak of validation of a kinetic mechanism in this section, we are referring to the comparison between predictions and experiment based on smog chamber studies. The second and more complex of the two parts, validation of the kinetic mechanism in the presence of transport processes (convection and turbulent diffusion), will be discussed in Chapter III.

To provide a framework for the discussion of kinetic mechanisms, we will first consider the highly generalized kinetic scheme given below.

$$
\begin{aligned}
NO_2 + h\nu &\xrightarrow{1} NO + O \\
O + O_2 + M &\xrightarrow{2} O_3 + M \\
O_3 + NO &\xrightarrow{3} NO_2 + O_2 \\
O_3 + \text{Hydrocarbons} &\xrightarrow{4} \text{Stable Products} + \text{Radicals} \\
\text{Radicals*} + \text{Hydrocarbons} &\xrightarrow{5} \text{Stable Products} + \text{Radicals}
\end{aligned}
$$

---

* "Radicals" include both O-atoms and OH radicals, the principal radical oxidizers of hydrocarbons.

$$\text{Radicals} + \text{NO} \xrightarrow{6} \text{Radicals} + \text{NO}_2$$

$$\text{Radicals} + \text{NO}_2 \xrightarrow{7} \text{Stable Products}$$

$$\text{Radicals} + \text{Radicals} \xrightarrow{8} \text{Stable Products}$$

The reactions that take place in the generation of photochemical smog, as exemplified by the above mechanism, can be classified as follows (in the terminology of chain reactions):

1. Initiation reactions - those that provide free radicals to induce chain reactions, e.g., $NO_2 + h\nu \rightarrow NO + O$*
2. Branching reactions - those in which there is a net increase in radical species, e.g. $O + HC \rightarrow$ Products + Radicals, where more than one radical results.
3. Propagation reactions - those in which there is no net gain or loss of radicals, but merely a change in identity, e.g. Radical + $HC \rightarrow$ Product + Radical.
4. Termination reactions - those that remove free radicals through the formation of stable end products, e.g. reactions 7 and 8.

---

* This reaction is not the only initiation reaction that occurs in the generation of smog. Photolysis of nitrous acid, alkyl nitrites and aldehydes also provide free radicals. For simplicity, and because $NO_2$ photolysis is the most important initiation reaction, we have omitted others in this generalized mechanism.

Let us now examine the behavior of this highly generalized mechanism to see if it is capable of predicting the qualitative features of the photochemical smog system, in particular, the rapid rate of conversion of NO to $NO_2$ and the effect of varying initial reactant concentrations on $O_3$ formation. In the discussion that follows, we denote the total concentration of radicals as [R] and that of hydrocarbons as [HC]. We can write a material balance on the total concentration of free radicals in the following manner:

$$\frac{d[R]}{dt} = a[NO_2] + b[HC][R] - c[NO_2][R] - d[R]^2$$

where the terms on the right hand side have the following significance:

$a[NO_2]$ = production of O-atoms by reaction 1

$b[HC][R]$ = the net rate of production of radicals from reactions 4 and 5

$c[NO_2][R]$ = the net depletion of radicals by reaction 7

$d[R]^2$ = the net depletion of radicals by reaction 8

The symbols a,b,c,d represent the combination of appropriate rate constants and stoichiometric coefficients.

We can identify two limiting cases of interest:

1. Near $t = 0$ when $[R] = 0$, i.e.

$$\frac{d[R]}{dt} = a[NO_2]$$

From this we can see that initially the concentration of free radicals increases at a rate proportional to the $NO_2$ concentration. Presumably, most of these radicals are oxygen atoms.

2. When the total radical population reaches a steady state (ss), $d[R]/dt = 0$. At this point

$$0 = a[NO_2] + b[HC][R] - c[NO_2][R] - d[R]^2$$

For case 2 we can examine the effect on $[R]_{ss}$ of the relative concentrations of $NO_2$ and HC. When $[NO_2] \gg [HC]$,

$$\frac{d[R]}{dt} = 0 = a[NO_2] - c[NO_2][R]_{ss}$$

or $[R]_{ss}$ is a constant a/c, dependent only on the photolysis rate of $NO_2$ and the rate of termination with $NO_2$. When the rate of production by chain branching, $b[HC][R]$ equals the termination rate with $NO_2$, $c[NO_2][R]$, the steady state radical concentration is

$$[R]_{ss} = [a[NO_2]/d]^{1/2}$$

Finally, when $[HC] \gg [NO_2]$,

$$\frac{d[R]}{dt} = 0 = b[HC][R] - d[R]^2$$

so that $[R]_{ss} = b[HC]/d$.

Summarizing, at steady state the limits of total free radical concentrations are

$$\frac{a}{c} \leq [R]_{ss} \leq \frac{b\,[HC]}{d}$$

(high $NO_2$) (low $NO_2$)

Using these relationships, Johnston et al. (1970) have estimated that actual concentrations may be:

| $\frac{c[NO_2]}{b[HC]}$ | 10 | 1 | 0.1 |
|---|---|---|---|
| $[R]_{ss}$, ppm | $1.1\times10^{-4}$ | $2\times10^{-3}$ | $3.6\times10^{-2}$ |

Leighton (1961) estimated that in photooxidation of an olefin such as propylene, NO is converted to $NO_2$ at a rate of 0.04 ppm $min^{-1}$ by reactions of the type 6. This rate is consistent with the steady state radical concentrations just calculated. For example, using $[R] = 10^{-3}$ ppm, $[NO] = 0.1$ ppm and a rate constant for reaction 6 of 500 $ppm^{-1}min^{-1}$, the rate of conversion of NO to $NO_2$ is 0.05 ppm $min^{-1}$.

Aside from predicting the rapid conversion of NO to $NO_2$, a mechanism must also be capable of simulating the effect of different initial reactant ratios on product formation in the smog system, as illustrated in Figure 2. Let us consider the two cases of low and high $NO_2$ concentrations. The photochemical smog process is initiated by $NO_2$ with the rate of increase of the total radical population depending on the initial concentration of $NO_2$. The maximum concentration of $NO_2$ occurs when the rate of conversion of NO to $NO_2$ just equals the rate of termination of radicals by $NO_2$. If this maximum concentration of $NO_2$ is low (i.e. low total initial $NO_x$), the concentration of radicals reaches very high values. The radicals rapidly convert NO to $NO_2$, allowing ozone to form. As we increase the total initial $NO_x$, and hence the $NO_2$ concentration at its maximum, the amount of $O_3$ formed should increase up to a point. That point is the one at which radical removal by $NO_2$ is at least as fast as chain branching, i.e. $b[HC] = c[NO_2]$. As we continue to increase the initial $NO_x$, and hence the $NO_2$, the steady state radical concentration continues to decrease, as we have seen. The result is that the rate of ozone formation slows down. Nevertheless, if we wait long enough there will be a significant accumulation of $O_3$. Thus, if we consider $O_3$ formation only over a fixed time of irradiation, it will seem that increasing initial NO is a beneficial policy with respect to $O_3$ formation, when, in fact, what has really happened is that we have not waited long enough for the reaction to go to completion.

We can also examine the effect of initial reactant ratios on the maximum amount of $O_3$ formed during an irradiation. Consider first an experiment in which the concentration of initial $NO_x$ ($NO + NO_2$) is large compared to initial HC. Note that the relative amounts of NO and $NO_2$ will serve only to govern the time needed to convert the NO to $NO_2$ and should not affect the ultimate maximum $O_3$ concentration attained. Figure 2a illustrates the type of concentration/time curves to be expected when $[NO_x]_o >> [HC]_o$. We see that the hydrocarbon is expended before all the NO is converted to $NO_2$. Since an appreciable amount of NO remains after the hydrocarbon is depleted, no significant $O_3$ concentration can be reached. Consider next the opposite limit, namely $[NO_x]_o << [HC]_o$. In this case, the NO is rapidly converted to $NO_2$ with little expenditure of HC. As [NO] becomes small, $O_3$ can accumulate. However, because of the large concentration of HC, the reaction of $O_3$ and HC will prevent $[O_3]$ from becoming too large. This case is illustrated in Figure 2b. Finally, the intermediate case of $[HC]_o \approx [NO_x]_o$ can be expected to yield the largest $O_3$ concentration. Thus, if one considers the maximum $O_3$ concentration achieved, regardless of the time of irradiation, as a function of $[HC]_o/[NO_x]_o$, one will get a curve of the type shown in Figure 2c.

We have seen that the simplified mechanism presented early in this section can account for several of the qualitative features of the photochemical smog system. However, the mechanism is inadequate for quantitative predictions of concentration-time behavior in smog chamber systems and the atmosphere for two basic reasons:

1. Several important inorganic reactions involving NO, $NO_2$, $H_2O$ and CO need to be included, and
2. The mechanism lacks detail in the treatment of hydrocarbon and radical species.

In attempting to construct a mechanism capable of accurate prediction, each of these points must be carefully considered.

We now present a very brief survey of the important inorganic and hydrocarbon reactions in the photochemical smog system. Numerous reviews of these reactions are available (Leighton, 1961 ; Altshuller and Bufalini, 1971; Johnston et al., 1970), so that we will consider here only those elements of the chemistry important to the development of a kinetic mechanism.

### 1. Inorganic Reactions

The reactions in the system of $NO_x$, air, $H_2O$ and CO have received much attention. A survey of rate constant values reveals the following reactions to be of greatest importance:

$$\left.\begin{aligned} \mathrm{NO_2} + h\nu &\xrightarrow{1} \mathrm{NO} + \mathrm{O} \\ \mathrm{O} + \mathrm{O_2} + \mathrm{M} &\xrightarrow{2} \mathrm{O_3} + \mathrm{M} \\ \mathrm{O_3} + \mathrm{NO} &\xrightarrow{3} \mathrm{NO_2} + \mathrm{O_2} \end{aligned}\right\} \text{The } \mathrm{NO_2\text{-}NO\text{-}O_3} \text{ Cycle}$$

$$\left.\begin{aligned} \mathrm{O} + \mathrm{NO} + \mathrm{M} &\xrightarrow{4} \mathrm{NO_2} + \mathrm{M} \\ \mathrm{O} + \mathrm{NO_2} &\xrightarrow{5} \mathrm{NO} + \mathrm{O_2} \\ \mathrm{O} + \mathrm{NO_2} + \mathrm{M} &\xrightarrow{6} \mathrm{NO_3} + \mathrm{M} \end{aligned}\right\} \begin{array}{l}\text{Important Reactions of} \\ \text{O with Inorganic Species}\end{array}$$

$$\left.\begin{aligned} \mathrm{O_3} + \mathrm{NO_2} &\xrightarrow{7} \mathrm{NO_3} + \mathrm{O_2} \\ \mathrm{NO_3} + \mathrm{NO} &\xrightarrow{8} \mathrm{2NO_2} \\ \mathrm{NO_3} + \mathrm{NO_2} &\xrightarrow{9} \mathrm{N_2O_5} \\ \mathrm{N_2O_5} &\xrightarrow{10} \mathrm{NO_2} + \mathrm{NO_3} \\ \mathrm{N_2O_5} + \mathrm{H_2O} &\xrightarrow{11} \mathrm{2HNO_3} \end{aligned}\right\} \begin{array}{l}\text{The Chemistry of } \mathrm{NO_3}, \\ \mathrm{N_2O_5}, \text{ and } \mathrm{HNO_3}\end{array}$$

$$\left.\begin{array}{r} NO + HNO_3 \xrightarrow{12} HNO_2 + NO_2 \\ HNO_2 + HNO_3 \xrightarrow{13} H_2O + 2NO_2 \end{array}\right\} \text{Reactions of } HNO_3 \text{ with Inorganic Species}$$

$$\left.\begin{array}{r} NO + NO_2 + H_2O \xrightarrow{14} 2HNO_2 \\ 2HNO_2 \xrightarrow{15} NO + NO_2 + H_2O \\ HNO_2 + h\nu \xrightarrow{16} OH + NO \end{array}\right\} \text{Chemistry of } HNO_2$$

$$\left.\begin{array}{r} OH + NO_2 + M \xrightarrow{17} HNO_3 + M \\ OH + NO + M \xrightarrow{18} HNO_2 + M \\ OH + CO + (O_2) \xrightarrow{19} CO_2 + HO_2 \end{array}\right\} \text{Important Reactions of OH with Inorganic Species}$$

$$HO_2 + NO \xrightarrow{20} OH + NO_2 \quad \} \text{Oxidation of NO by } HO_2$$

$$H_2O_2 + h\nu \xrightarrow{21} 2OH \quad \} \text{Photolysis of } H_2O_2$$

We shall discuss several of these reactions further in Chapter IV, considering the degree of study they have received, the rates at which they proceed, and the uncertainty associated with the individual reaction rate constants.

### 2. Hydrocarbon Reactions

We first wish to make a fundamental distinction between types of mechanisms, based on the treatment of hydrocarbon and free radical reactions. The first type is that written for the photooxidation of a *specific hydrocarbon.* This is the type we ordinarily envision, one in which each species in each reaction represents a distinct chemical entity. The second type is the *lumped mechanism,* one which contains certain fictitious species which represent entire classes of reactants.

In many chemical systems the number of species is often extremely large. In addition, there is usually a significant range of reactivities of the species in systems of this type. Certain species may not be present in measurable concentrations and many rate constants may not be known accurately. As a result, quantitative predictions of reaction rates may be highly uncertain. In such a case, one is unable to deal with each species separately; rather, one may partition the species into a few classes (called lumped classes), and then consider each class as an independent entity. This idea has already been illustrated in the highly simplified general mechanism cited earlier, in which all hydrocarbons and free radicals were represented by HC and R, respectively.

General lumping theory in chemical kinetics has been the subject of several recent investigations. Wei and Kuo (1969a, 1969b) have presented a general lumping analysis of monomolecular, first order reacting mixtures. Hutchinson and Luss (1970), Luss and Hutchinson (1971), and Goli, Keri, and Luss (1972) have studied the lumping of reaction mixtures consisting of a large number of parallel, independent, and irreversible nth order reactions. In contrast to the work of Wei and Kuo, which was directed toward the determination of conditions under which exact lumping was possible, the studies of Luss have been concerned with the problem of predicting a priori the maximum error involved in lumping and with the type of species that should be lumped together to ensure that the prediction error is less than some given bound.

No theory has yet been developed that is concerned with the lumping of large sets of coupled, bimolecular reactions, such as occur in the generation of photochemical smog. We outline here some of the more important questions that must be addressed if we are to effectively model atmosphere photochemical reactions.

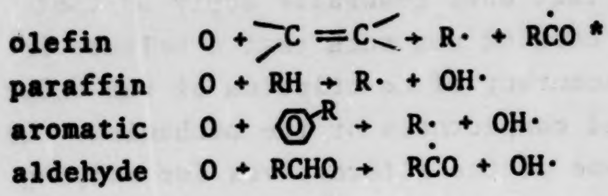
1. In the photochemical smog system the large number of hydrocarbons and free radicals makes lumping a necessity in developing a practical kinetic mechanism. However, which hydrocarbons should be lumped together and what criterion should be used to establish groupings? For example, should the lumping be carried out according to hydrocarbon class, such as paraffins, aromatics, olefins, etc., with respect to reactivity with O, $O_3$ and OH· regardless of class, or with regard to the number of free radical products?
2. Which free radicals should be lumped together and what criterion should be used to establish groupings? For example, should the lumping be carried out with respect to radical class such as alkyl, acyl, alkoxyl, etc., with respect to most probable chain length, or with respect to reactivity?
3. How are the lumped rate constants and stoichiometric coefficients to be determined?
4. Is the order of the reaction of the lumped hydrocarbon species the same as the individual reaction being represented?

The one guideline that does generally apply is that lumping should be carried out such that a balance is achieved between accuracy of description of the underlying processes and compactness of the mechanism. Let us now consider some of the alternatives for lumping in photochemical smog systems.

Given a distribution of atmospheric hydrocarbons, we must first identify and tabulate the reactions in which they may participate. Photochemical decomposition of primary hydrocarbon pollutants is unimportant, except perhaps for aldehydes; we must therefore focus our attention on thermal reactions. Of the active species that we have mentioned thus far, those capable of reacting with hydrocarbons include O, $O_3$, and OH. In this discussion we divide the primary hydrocarbons according to the classes--olefins, paraffins, aromatics and aldehydes--and examine the reactions of each with the three radical species. While these groupings are certainly not inclusive of all classes of hydrocarbons in the atmosphere, they comprise the major portion. The two basic aspects of an individual reaction that we will consider are: (1) the product distribution and (2) the rate constant.

### a. Atomic Oxygen - Hydrocarbon Reactions

The principal products of O atom hydrocarbon reactions are summarized below:



olefin $O + \rangle C{=}C\langle \rightarrow R\cdot + R\dot{C}O$ *

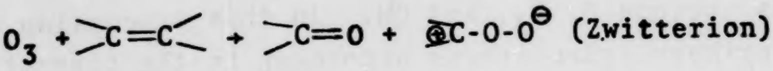
paraffin $O + RH \rightarrow R\cdot + OH\cdot$

aromatic $O + \bigcirc\!\!-R \rightarrow \dot{R}\cdot + OH\cdot$

aldehyde $O + RCHO \rightarrow R\dot{C}O + OH\cdot$

b. Ozone-Hydrocarbon Reactions

Only olefins, among the four hydrocarbon groupings we are considering, are attacked readily by ozone in the vapor phase. The so-called Criegie mechanism for $O_3$ addition to olefins can be summarized as



$O_3 + \rangle C{=}C\langle \rightarrow \rangle C{=}O + {}^{\oplus}C\text{-}O\text{-}O^{\ominus}$ (Zwitterion)

The products are thus a carbonyl and an unstable intermediate called a zwitterion, the subsequent reactions of which are not very well known. Possible decomposition reactions of the zwitterion are

$$R_1R_2COO \rightarrow R_1R_2 + CO_2$$

$$HRCOO \rightarrow ROH + CO$$

$$HRCOO \rightarrow RO\cdot + H\dot{C}O$$

$$HRCOO \rightarrow R\dot{C}O + OH\cdot$$

In addition, the zwitterion may participate in reactions with $O_2$, NO or $NO_2$:

---

* If one of the carbons on the double bond is external, both HCO and $R\dot{C}O$ can form.

$$>C\text{-}O\text{-}O + A \rightarrow >C{=}O + AO \quad (A = O_2,\ NO \text{ or } NO_2)$$

If this reaction predominated we would expect a yield of two carbonyl compounds per olefin. Actually, a yield between 1 and 1.4 is observed. In general, then, a stable carbonyl and two free radicals are formed through the $O_3$-olefin reaction. We might note, however, that the dynamics of this class of reactions are still not fully understood. We shall return to $O_3$-olefin reactions in Chapter III where we discuss reactions needing further experimental investigation to elucidate product distributions.

### c. Hydroxyl Radical - Hydrocarbon Reactions

Hydroxyl radicals react with hydrocarbons either by abstracting a hydrogen atom or by addition. For paraffins the reaction is known to be

$$RH + OH\cdot \rightarrow R\cdot + H_2O$$

At this time there are no reported product data for OH/olefin or OH/aromatic reactions, although it is known that the propylene reaction proceeds via addition to the double bond to form a radical. If this is the case with other olefins, we would expect one free radical as a product,

$$>C{=}C< + OH\cdot \rightarrow R\cdot^{*}$$

Aldehyde/OH reactions also yield one free radical,

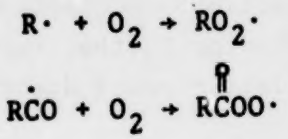
$$HCHO + OH\cdot \rightarrow H_2O + \dot{H}CO$$

---

* The actual structure of this radical would be $HO\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot$

### 3. Free Radical Reactions

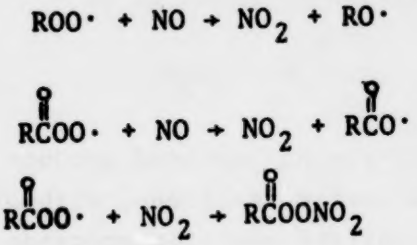
As we have just seen, the reactions of O, $O_3$, and OH· with hydrocarbons yield the following classes of free radicals: R·, RCO, RO·, where R can be a hydrogen atom, an alkyl group, or an alkyl group containing an alcohol functional group. We must now trace the most likely reactions of these species with the others in the system. Consider R·, $R\dot{C}O$ and OH· as typical products. Both R· and $R\dot{C}O$ will most probably react with $O_2$ by



$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$R\dot{C}O + O_2 \rightarrow R\overset{O}{\overset{\|}{C}}OO\cdot$$

These peroxy radicals will undergo a variety of reactions, the most important of which are with NO and $NO_2$

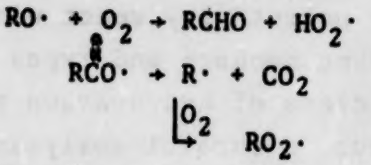


$$ROO\cdot + NO \rightarrow NO_2 + RO\cdot$$

$$R\overset{O}{\overset{\|}{C}}OO\cdot + NO \rightarrow NO_2 + R\overset{O}{\overset{\|}{C}}O\cdot$$

$$R\overset{O}{\overset{\|}{C}}OO\cdot + NO_2 \rightarrow R\overset{O}{\overset{\|}{C}}OONO_2$$

The two new radicals formed will then probably react in the following manner:

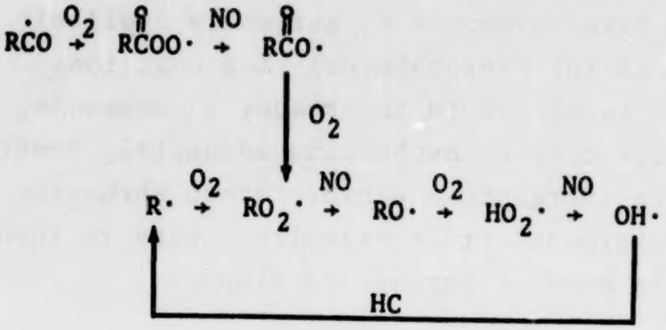


$$RO\cdot + O_2 \rightarrow RCHO + HO_2\cdot$$

$$R\overset{O}{\overset{\|}{C}}O\cdot \rightarrow R\cdot + CO_2$$

$$R\cdot \xrightarrow{O_2} RO_2\cdot$$

The likely history of typical alkyl and acyl radicals in chain propagation reactions can thus be depicted as



We see that, during the lifetimes of R· and $\dot{R}CO$, many molecules of NO can be converted to $NO_2$ (of course, each step in the sequence competes with other propagation and termination reactions). When NO concentration becomes sufficiently low, one possibility is that the peroxyacyl radicals will react with $NO_2$ to give peroxy acyl nitrates. The alkoxyl radicals may also react with $NO_2$ at this point to yield alkyl nitrates.

Now the problem of representing hydrocarbon and free radical reactions should be somewhat clearer. In a complex mixture of hydrocarbons, such as is observed in the atmosphere, we might divide the total hydrocarbon population into n lumped hydrocarbon species, $HC_1$, $HC_2$,..., $HC_n$. Each of these may potentially react with O, $O_3$, and OH, yielding varying numbers and types of free radicals depending on the class of hydrocarbon participating in the reaction. Thus, a careful analysis of lumping alternatives is a necessary step in the development of a generalized kinetic mechanism. In Section D we undertake such an analysis. However, before going to this, we present a brief synopsis of currently available kinetic mechanisms for photochemical smog reactions. This review should be of aid to the reader in assessing the extent to which current mechanisms adequately treat the details of the inorganic and hydrocarbon chemistry. With this background, it is relatively easy to identify those areas in need of further development.

## C. Current Photochemical Kinetic Mechanisms

It is only in the last ten years that general kinetic mechanisms have been postulated to describe photochemical smog chemistry. The mechanisms that have been proposed can be classified as either *specific* (written for photooxidation of a specific hydrocarbon) or *lumped* (written for one or more species involving lumped reactants) and include the following:

Specific Mechanisms

| | |
|---|---|
| Westberg and Cohen (1969) | isobutylene |
| Behar (1970) | propylene |
| Hecht and Seinfeld (1972) | propylene |
| Niki et al. (1972) | propylene |
| Demerjian et al. (1973) | propylene<br>trans-2-butene<br>isobutene<br>n-butane, and<br>formaldehyde |

## Lumped Mechanisms*

Eschenroeder and Martinez (1972)
Wayne et al. (1971)
Hecht and Seinfeld (1972)

Specific mechanisms, while often quite complex (e.g. the Hecht and Seinfeld propylene mechanism contains 81 reactions), can play an important role as an aid in understanding the fundamental chemistry of the photooxidation process. However, for none of the specific mechanisms listed above has there been reported a program of validation over a range of initial reactant concentrations. Thus, all five can only be considered at this point as detailed chemical speculations for the specific hydrocarbon system.

Assuming, however, that validated versions of specific mechanisms are available, these mechanisms would still not be suitable for inclusion in an urban airshed model. The main reason for this centers on the philosophy underlying the development of such mechanisms. The decision to develop and implement a specific mechanism implies the desire to represent reaction processes as accurately as is feasible. Thus, a relatively large number of reaction steps must be incorporated in a description of the dynamics of consumption of *a particular hydrocarbon,* such as propylene. Reaction dynamics will, however, vary for the many hydrocarbon species present in the atmosphere. If, for example, thirty to forty steps are required to describe propylene kinetics, and fifty hydrocarbon species, each having unique dynamics, are believed to exert a significant impact on atmospheric reaction processes, one is faced with an intractable representation of the system. Alternatively, adoption of a detailed representation of the reactions of a single species (for example, propylene) which may, upon development, be applied to a single, generalized hydrocarbon is tantamount to constructing a mechanism having many of the representational deficiencies of a lumped kinetic scheme and, in addition, introduces a substantial parameter estimation problem.

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* Three lumped mechanisms, nearly identical in structure, were developed at an early stage by Eschenroeder (1969), Friedlander and Seinfeld (1969) and Behar (1970). (Eschenroeder's mechanism, slightly modified, is substantially the same as, or superior to, those of Friedlander and Seinfeld and Behar). For the obvious reasons of simplicity and convenience, it would be desirable to adopt such mechanisms for general use. However these mechanisms not only omit steps now known to be important, but they were never successfully validated over a range of initial conditions. All three have since been either abandoned or modified.

Each of the three lumped mechanisms listed above is currently in use in programs of mathematical modeling of photochemical smog in the Los Angeles basin. Detailed discussions of each are readily available in the original references. We note, however, that the mechanisms of Eschenroder and Martinez and Hecht and Seinfeld are very similar. Table I presents a comparison of the two mechanisms. The EM differs from the HS mechanism in the treatment of $HNO_3$ and $HNO_2$, the inclusion of CO, and the treatment of $HO_2$.

## TABLE 1. The Hecht-Seinfeld (HS) and Eschenroeder-Martinez (EM) Mechanisms

### HS

$$NO_2 + h\nu \xrightarrow{1} NO + O$$

$$O + O_2 + M \xrightarrow{2} O_3 + M$$

$$O_3 + NO \xrightarrow{3} NO_2 + O_2$$

$$O_3 + NO_2 \xrightarrow{4} NO_3 + O_2$$

$$NO_3 + NO \xrightarrow{5} 2NO_2$$

$$NO_3 + NO_2 \xrightarrow[6]{H_2O} 2HNO_3$$

$$NO + NO_2 \xrightarrow[7]{H_2O} 2HNO_2$$

$$2HNO_2 \xrightarrow{8} NO + NO_2 + H_2O$$

$$HNO_2 + h\nu \xrightarrow{9} OH + NO$$

$$CO + OH \xrightarrow[10]{O_2} CO_2 + HO_2$$

$$HO_2 + NO \xrightarrow{11} OH + NO_2$$

$$HO_2 + NO_2 \xrightarrow{12} HNO_2 + O_2$$

$$O + HC \xrightarrow{13} \alpha RO_2$$

$$OH + HC \xrightarrow{14} \beta RO_2$$

$$O_3 + HC \xrightarrow{15} \gamma RO_2$$

$$RO_2 + NO \xrightarrow{16} NO_2 + \epsilon OH$$

$$RO_2 + NO_2 \xrightarrow{17} PAN$$

$$O + HC_2 \xrightarrow{18} \alpha_2 RO_2$$

$$OH + HC_2 \xrightarrow{19} \beta_2 RO_2$$

$$O_3 + HC_2 \xrightarrow{20} \gamma_2 RO_2$$

$$NO_2 \xrightarrow{21} \text{WALL OR PARTICLE}$$

### EM

$$NO_2 + h\nu \xrightarrow{1} NO + O$$

$$O + O_2 + M \xrightarrow{2} O_3 + M$$

$$O_3 + NO \xrightarrow{3} NO_2 + O_2$$

$$OH\cdot + NO_2 + M \xrightarrow{4} HNO_3 + M$$

$$NO + NO_2 \xrightarrow[5]{H_2O} 2HNO_2$$

$$HNO_2 + h\nu \xrightarrow{6} OH\cdot + NO$$

$$OH\cdot + NO + M \xrightarrow{7} HNO_2 + M$$

$$O + HC \xrightarrow{8} b_1(RO_2)$$

$$OH + HC \xrightarrow{9} b_2(RO_2)$$

$$O_3 + HC \xrightarrow{10} b_3(RO_2)$$

$$RO_2 + NO \xrightarrow{11} NO_2 + d(OH)$$

$$RO_2 + NO_2 \xrightarrow{12} c(PAN)$$

**TABLE 2. Wayne et al. Mechanism**

$$NO_2 + h\nu \xrightarrow{1} NO + O$$

$$O + O_2 + M \xrightarrow{2} O_3 + M$$

$$O_3 + NO \xrightarrow{3} NO_2 + O_2^*$$

$$NO_2 + O_3 \xrightarrow{4} NO_3 + O_2$$

$$NO_3 + NO \xrightarrow{5} 2NO_2$$

$$C_2H_4O_2 + O_2 \xrightarrow{6} CH_3CHO + O_3$$

$$NO + HO_2 \xrightarrow{7} NO_2 + OH$$

$$H + O_2 + M \xrightarrow{8} HO_2 + M$$

$$DUMHC + O_2^* \xrightarrow{9} CH_3OOH$$

$$O_2^* \xrightarrow{10} O_2$$

$$CH_3OOH + h\nu \xrightarrow{11} CH_3O + OH$$

$$NO_2 + OH \xrightarrow{12} HNO_3$$

$$OH + O_3 \xrightarrow{13} HO_2 + O_2$$

$$OH + CO \xrightarrow{14} H + CO_2$$

$$CH_3 + O_2 + M \xrightarrow{15} CH_3O_2 + M$$

$$CH_3O_2 + NO \xrightarrow{16} CH_3O + NO_2$$

$$CH_3O + O_2 + NO \xrightarrow{17} CH_3O_2 + NO_2$$

$$C_2H_3O + O_2 + NO \xrightarrow{18} C_2H_3O_2 + NO_2$$

$$C_2H_3O_2 + NO \xrightarrow{19} C_2H_3O + NO_2$$

$$C_2H_4O_2 + NO \xrightarrow{20} CH_3CHO + NO_2$$

$$CH_3O + O_2 \xrightarrow{21} HCHO + HO_2$$

**TABLE 2. (Continued) Wayne et al. Mechanism**

$$C_3H_6 + O \xrightarrow{22} CH_3 + C_2H_3O$$

$$C_3H_6 + O_3 \xrightarrow{23} HCHO + C_2H_4O_2$$

$$C_3H_6 + O + O_2 \xrightarrow{24} HCHO + C_2H_4O_2$$

$$C_3H_6 + O_2^* \xrightarrow{25} CH_3O + C_2H_3O$$

$$C_3H_6 + HO_2 \xrightarrow{26} CH_3O + CH_3CHO$$

$$C_3H_6 + CH_3O_2 \xrightarrow{27} CH_3 + CH_3O + C_2H_3O$$

$$C_2H_3O + M \xrightarrow{28} CH_3 + CO + M$$

$$CH_3O + NO_2 \xrightarrow{29} CH_3ONO_2$$

$$C_2H_3O + O_2 + NO_2 \xrightarrow{30} C_2H_3O_3NO_2$$

$$DUMHC + O \xrightarrow{31} CH_3 + C_2H_3O$$

$$HCHO + h\nu \xrightarrow{32} H + H + CO$$

$$NO_2 + NO_3 + H_2O \xrightarrow{33} 2HNO_3$$

While the EM and HS mechanisms are quite similar, the third in current use, that of Wayne et al., given in Table 2, adopts an inherently different approach. The mechanism is based on the photooxidation of propylene, and its application to atmospheric photochemistry is presumably based on the assumption that the mixture of atmospheric hydrocarbons behaves as a binary mixture of propylene and a second, relatively unreactive, hydrocarbon. This assumption is in contrast to that inherent to the EM and HS mechanisms, i.e. that the atmospheric hydrocarbon mixture can be represented by two lumped hydrocarbon species, one more reactive than the other, neither of which represents a specific hydrocarbon. Because of the inclusion of detailed propylene chemistry in the Wayne mechanism, many specific radical species have been included, whereas only one lumped radical species (aside from O and OH·)* appears in the EM and HS mechanisms. In the validation exercises reported, the two lumped hydrocarbons in the EM and HS mechanisms have been specified on the basis of reactivity. As we shall see, when hydrocarbons are lumped on this basis, it is difficult to ascribe precise values to the generalized stoichiometric coefficients.

We now present a systematic analysis of hydrocarbon and radical lumping in order to illustrate the various levels of complexity that might be included in a mechanism and to identify the decisions which must be made in constructing a lumped mechanism.

## D. The Evolution of a Lumped Mechanism

As we have noted, the primary problem in the development of a lumped mechanism is the representation of the hydrocarbon and free radical reactions. In this section we shall give some indication as to the options available in this representation.

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* If CO is present, $HO_2\cdot$ is retained as a separate species in the HS mechanism.

### 1. Lumping of Hydrocarbons

Consider first the question of the lumping of hydrocarbons. Our objective is to form a small number of groups of lumped hydrocarbon species which will represent the mixture of hydrocarbons present in the atmosphere. Alternative criteria are available by which to form the hydrocarbon groupings, for example:

1. Lump hydrocarbons based on *class* (olefins, aromatics, paraffins, etc.).
2. Lump hydrocarbons based on *reactivity* with individual oxidants, such as O, $O_3$ or OH·.

Let us discuss the implications of each of these two lumping criteria. Consider criterion 1, the lumping of hydrocarbons by class. For example, let

$HC_1$ = olefins
$HC_2$ = aromatics
$HC_3$ = paraffins
$HC_4$ = aldehydes

Although the mechanisms for the oxidation of these four classes of hydrocarbons by O, OH, and $O_3$ have not yet been resolved in detail, the likely product distributions are:

$$HC_1 + \begin{cases} O \overset{k_1}{\rightarrow} R\cdot + R\dot{C}O \\ O_3 \overset{k_1'}{\rightarrow} R\dot{C}O + RO\cdot + RCHO \\ OH\cdot \overset{k_1''}{\rightarrow} R\cdot\,^{*} \end{cases}$$

---

* OH adds to the double bond of olefins forming an alcohol-like free radical, $R\underset{OH}{C}H\dot{C}H_2$, which we have assumed to react in the same fashion as an alkyl radical. This is not exactly true, as this free radical decomposes in a different manner than R· in subsequent reactions. Specifically, $RCHOH\dot{C}H_2$ is thought to react to form one additional aldehyde (Niki et al., 1972). We have, therefore, included $HC_4$ as a product of the OH-$HC_1$ elementary reaction in Table 4 to correct for this anomaly.

$$HC_2 + \begin{cases} O & \xrightarrow{k_2} R\cdot + OH\cdot \\ O_3 & \xrightarrow{k_2'} \text{not important} \\ OH\cdot & \xrightarrow{k_2''} R\cdot + H_2O \end{cases}$$

$$HC_3 + \begin{cases} O & \xrightarrow{k_3} R\cdot + OH\cdot \\ O_3 & \xrightarrow{k_3'} \text{not important} \\ OH\cdot & \xrightarrow{k_3''} R\cdot + H_2O \end{cases}$$

$$HC_4 + \begin{cases} O & \xrightarrow{k_4} R\dot{C}O + OH\cdot \\ O_3 & \xrightarrow{k_4'} \text{not important} \\ OH\cdot & \xrightarrow{k_4''} R\dot{C}O + H_2O \\ h\nu & \xrightarrow{k_4'''} R\dot{C}O^{*} + H\cdot + CO \end{cases}$$

Since the number of free radical products resulting from O, $O_3$ and OH· attack on each lumped species is essentially the same for all individual hydrocarbon members of each lumped grouping, (i.e. OH· attack on all paraffins is expected to yield one alkyl radical) the number and type of free radical products in each step shown above can be specified with some certainty. On the other hand, within each lumped species there is a distribution of rate constants for the reactions with O, $O_3$ and OH·. For example, within $HC_1$ there is a wide spectrum of rate constants for olefin-O reactions. Therefore, the rate constants for O, $O_3$ and OH· reactions with each lumped species must be taken as average values which reflect in some manner the relative amounts of different individual species within each lumped species. Since the differing reactivities of the individual components comprising a grouping will lead to their disappearance at different rates throughout the course of photooxidation, the effective rate constants for reaction of the lumped species with O, $O_3$ and OH· must also vary during the course of the reaction. In summary, then, lumping of hydrocarbons by class will allow rather definite assignment of stoichiometric coefficients but will necessitate rate constants which reflect the average reactivity of the individual species within each lumped species as a function of time.

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* If $HC_4$ is HCHO, $H\dot{C}O$ (which decomposes to H· + CO), rather than $R\dot{C}O$, forms.

We now consider criterion 2, the lumping of hydrocarbons by reactivity. The first question we face in this case is - reactivity with respect to what? The three obvious choices are reactivity (rate constant) with O, $O_3$ and OH·. Perhaps the most logical species among the radicals O, $O_3$ and OH upon which to base the reactivity grouping is that species which is most responsible for hydrocarbon disappearance in photooxidation experiments. Computed rates of hydrocarbon disappearance by O, $O_3$ and OH generally confirm that the OH-rate is the most important of the three, except at the very beginning of the photooxidation when the O-atom rate is predominant.

Table 3 presents rate constants relative to that of propylene for the reactions of several hydrocarbons with O, $O_3$ and OH, together with the relative reactivities of these hydrocarbons based on NO-$NO_2$ conversion rates observed experimentally (Altshuller and Cohen, 1963; Glasson and Tuesday, 1970). We see that the OH-hydrocarbon rate constants correlate quite well with reactivities for all classes of hydrocarbons listed in the table. On the other hand, O-atom and $O_3$ rates correlate with reactivities only for the olefinic compounds. For the aromatics, aldehydes and alkanes, the O-atom and $O_3$ rate constants are small compared with the measured reactivies. Since the most important role played by OH is that of generating organic free radicals for conversion of NO to $NO_2$, it would appear that lumping of hydrocarbons with respect to their OH reaction rate constant would be the most consistent with measured hydrocarbon reactivities. Suppose, for example, that we elect to divide the hydrocarbon mixture into three classes based on their OH rate constant:

$HC_1$ $\quad k < 1000\ \text{ppm}^{-1}\text{min}^{-1}$
$HC_2$ $\quad 1000 < k < 5000\ \text{ppm min}^{-1}$
$HC_3$ $\quad k > 5000\ \text{ppm}^{-1}\text{min}^{-1}$

On this basis each group would contain all classes of hydrocarbons, with the rate constants for reaction with OH defined by the composition of the grouping. Rate constants for reaction with O and $O_3$, however, would not necessarily correlate with the grouping based on the OH rate and would have to be determined in a manner similar to the case of lumping with respect to hydrocarbon class. However, during the main course of the reaction, the hydrocarbons within each group would be consumed at roughly the same rate so that the reactivity and stoichiometry of the group would not be expected to change with time. In the late stages of the photooxidation, $O_3$-hydrocarbon reactions become quite important. This raises a potential problem for lumping on the basis of the OH rate.

While rate constants can be determined relatively accurately, the number and types of free radical products within each lumped group would vary because each group would contain hydrocarbons of all classes. This would necessitate the adoption of stoichiometric coefficients which reflect the individual makeup of each lumped group.

To illustrate the forms of lumped reactions following the scheme based on OH-reactivity, let us assume we have N groups, as, for example, the three defined above $HC_1$, $HC_2$, $HC_3$. The reactions with O, $O_3$ and OH can be written:

$$HC_i + \begin{cases} O \xrightarrow{k_i} \alpha_{i1}R\cdot + \alpha_{i2}R\dot{C}O + \alpha_{i3}OH\cdot \\ O_3 \xrightarrow{k_i'} \beta_{i1}R\dot{C}O + \beta_{i2}RO\cdot + \beta_{i3}RCHO \\ OH \xrightarrow{k_i''} \gamma_{i1}R\cdot + \gamma_{i2}R\dot{C}O \end{cases}$$

$$i = 1,2,\ldots,N$$

where $\alpha_{ij}$, $\beta_{ij}$ and $\gamma_{ij}$ are stoichiometric coefficients which reflect the individual compositions of the $HC_i$, $i = 1,2,\ldots,N$. For example, if $HC_1$ consisted entirely of olefins we might expect $\alpha_{i1} = \alpha_{i2} = 1$ and $\alpha_{i3} = 0$. Thus, the stoichiometric coefficients are *not* to be considered as freely adjustable parameters, but rather as parameters whose values are fixed because of the choice of hydrocarbons comprising each lumped species $HC_i$.

## TABLE 3.

### Relative Rate Constants and "Smog Reactivity"*

| Compound | Relative Rate Constants | | | Reactivity** |
|---|---|---|---|---|
| | O | $O_3$ | OH | |
| **Olefins** | | | | |
| Propylene | 1.0 | 1.0 | 1.0 | 1.0 |
| Ethylene | 0.2 | 0.3 | 0.1 | 0.3 |
| Isobutene | 4.4 | 1.7 $\sim$ 2 | 2.5 | 1 |
| Trans-2-Butene | 4.9 | 2.8 $\sim$ 36 | 4.2 | 4 |
| 2-Methyl-2-Butene | 14 | 2.4 | 7.1 | 6 |
| Tetramethylethylene | 18 | 3.9 $\sim$ 62 | 8.6 | 17 |
| **Aromatics** | | | | |
| Benzene | .007 | --- | $\leq$ 0.05 | 0.1 |
| Xylene | --- | < 0.2 | 1.1 | 1 |
| **Aldehydes** | | | | |
| Formaldehyde | 0.05 | --- | 0.9 | 0.7 |
| Acetaldehyde | .15 | --- | 0.9 | 0.7 |
| Proprionaldehyde | $\sim$ .2 | --- | 1.8 | 2 |
| **Alkanes** | | | | |
| n-Butane | .008 | --- | 0.24 | 0.2 |

* Source of Table: Niki et al. (1972).

** Based on the rate of conversion of NO to $NO_2$

Let us summarize the advantages and disadvantages of the two alternative hydrocarbon lumping crtieria. For *lumping by hydrocarbon class:*

Advantages -

1. The definition of the lumped species depends only on the type of hydrocarbon (i.e. olefin, aromatic, alkane, etc.).
2. Since the products of O, $O_3$ and OH reactions with various hydrocarbon classes are essentially the same within each class, the number and type of free radical products would be well-defined for each class (assuming the products are indeed known).

Disadvantages -

1. The rate constants for reaction with O, $O_3$ and OH vary for the individual components in each lumped species necessitating the computation of "average" rate constants.
2. The relative distribution of the hydrocarbons in each lumped species will change throughout the course of the photooxidation necessitating a change in "average" rate constants with time.

For *lumping by hydrocarbon reactivity* (with OH):

Advantages -

1. The definition of the lumped species would correspond closely to the role played by the individual hydrocarbons comprising it in the conversion of NO to $NO_2$.

2. Since the reactivity of each lumped species is roughly invariant in time, rate constants and stoichiometric coefficients for the lumped OH-HC reaction would not require adjustment during the course of the reaction.

Disadvantages -

1. Each grouping would contain hydrocarbons of all classes, making it difficult to account for the distribution of free radicals produced as a result of reactions with O, $O_3$ and OH.
2. In the late stages of the photooxidation, ozonolysis reactions assume a level of importance equal to or greater than that of OH. A lumping on the basis of OH reactivity may no longer reflect the reactivity distribution of the total mixture at that stage.

Neither mode of hydrocarbon lumping appears overwhelmingly superior to the other. Nevertheless, lumping by hydrocarbon class seems to offer several advantages over lumping by reactivity. First, fewer stoichiometric coefficients need be specified in the former method, thereby leading to fewer unspecified parameters. Second, rate constant values for hydrocarbon-OH reactions are in many cases not known precisely enough to permit a clear distinction to be made among hydrocarbons as to reactivity class. Third, atmospheric measurements are made according to hydrocarbon class, and lumping by class would enable direct comparisons of mechanism predictions with atmospheric data. For these reasons, we will subsequently employ hydrocarbon lumping by class in our development of a general mechanism.

## 2. Lumping of Radicals

The second aspect of the overall lumping problem is the representation of free radicals. The two extremes in the representation of radicals are the specific mechanisms in which no lumping is used (each radical species is a distinct entity) and the qualitative mechanism employed earlier in which all free radicals were combined into a single species R. The first limit is unrealistic from a computational point of view and also in light of our incomplete knowledge of free radical rate constants. In contrast, the other limit does not afford us the ability to distinguish the effect of different hydrocarbon mixtures on the concentration/time behavior of a specific system. Therefore, we seek a basis for the lumping of radicals that lies somewhere between these two extremes.

A detailed study of free radical reactions in photochemical smog (Leighton, 1961) indicates that radicals of similar structure usually undergo similar reactions at roughly comparable rates. This suggests that the most detailed representation of radicals would involve having separate species for each radical class. The classes of radicals involved have already been introduced. They are

| | |
|---|---|
| $R\cdot$ | alkyl |
| $R\dot{C}O$ | acyl |
| $ROO\cdot$ | peroxyalkyl (including $HO_2\cdot$) |
| $R\overset{O}{\overset{\|}{C}}OO\cdot$ | peroxyacyl |
| $R\overset{O}{\overset{\|}{C}}O\cdot$ | acylate |
| $RO\cdot$ | alkoxyl (including $OH\cdot$) |

In an earlier section we listed several of the most probable reactions involving these radicals that would take place in a hydrocarbon-$NO_x$-air system. We also illustrated typical histories of acyl and alkyl radicals in such a system. Based on these likely reactions, we wish to propose a lumping scheme which is consistent with the probable chain lengths of each radical (and thus the conversion rate of NO to $NO_2$).

i) Alkyl radicals - We assume that alkyl radicals quickly add $O_2$ to form peroxyalkyl radicals. Thus $ROO\cdot$, and not $R\cdot$, need specifically enter into the mechanism.

ii) Acyl radicals - We assume that acyl radicals, like alkyl radicals, quickly add $O_2$ to form peroxyacyl radicals. Thus, $R\overset{O}{\overset{\|}{C}}OO\cdot$, and not $R\dot{C}O$, need specifically enter into the mechanism.

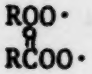
iii) Peroxyalkyl radicals - These radicals undergo reaction with NO to form $NO_2$. Thus, they remain in the mechanism. Because of the importance of $HO_2\cdot$ we remove it from the class $ROO\cdot$ and treat it as a separate species.

iv) Peroxyacyl radicals - Like $ROO\cdot$, these can react with both NO and $NO_2$. They are included in the mechanism.

v) Acylate radicals - These radicals result from reaction of NO and peroxyacyl radicals. We assume that they decompose quickly to form alkyl radicals (hence, peroxyalkyl radicals) and $CO_2$. Thus, they are not included in the mechanism.

vi) Alkoxyl radicals - These radicals result from reaction of peroxyalkyl radicals with NO and from ozonolysis of olefins and enter into reactions with NO and $NO_2$ to form stable products. The most important member of this class is the hydroxyl radical. Because of the extreme importance of OH, it seems desirable to remove OH from the RO class and retain each in the mechanism.

Summarizing, the radicals which appear to be of sufficient importance to warrant separate treatment are:

$ROO\cdot$ (excluding $HO_2\cdot$)

$R\overset{\overset{O}{\|}}{C}OO\cdot$
$RO\cdot$ (excluding $OH\cdot$)
$OH\cdot$
$HO_2\cdot$

## 3. Formulation of a Lumped Mechanism

The purpose of this section is to present the combined conclusions of the previous two sections in a manner illustrative of the development of a lumped mechanism. In particular, we will employ the lumping scheme suggested for hydrocarbon in section 1 and the categorization of radicals described in section 2.

We first rewrite the hydrocarbon reactions so as to correspond to the preferred lumping criterion, namely by hydrocarbon class:

$HC_1$ = olefins
$HC_2$ = aromatics
$HC_3$ = paraffins
$HC_4$ = aldehydes

$$HC_1 + O \rightarrow ROO\cdot + \alpha R\overset{O}{\overset{\|}{C}}OO\cdot + (1 - \alpha)\, HO_2\cdot$$

$$HC_1 + O_3 \rightarrow R\overset{O}{\overset{\|}{C}}OO\cdot + RO\cdot + HC_4$$

$$HC_1 + OH\cdot \rightarrow ROO\cdot$$

$$HC_2 + O \rightarrow ROO\cdot + OH\cdot$$

$$HC_2 + OH\cdot \rightarrow ROO\cdot + H_2O$$

$$HC_3 + O \rightarrow ROO\cdot + OH\cdot$$

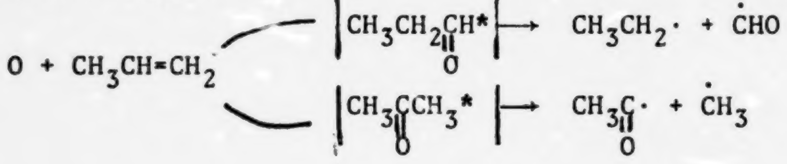
$$HC_3 + OH\cdot \rightarrow ROO\cdot + H_2O$$

$$HC_4 + O \rightarrow R\overset{O}{\overset{\|}{C}}OO\cdot + OH\cdot$$

$$HC_4 + OH\cdot \rightarrow \beta R\overset{O}{\overset{\|}{C}}OO\cdot + (1 - \beta)\, HO_2\cdot + H_2O$$

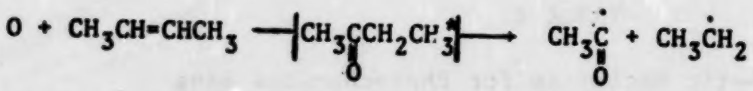
$\alpha$ is the fraction of carbon atoms attached to the double bond in a mono-olefin which are not terminal atoms on the chain; thus, this fraction can be specified a priori. $\beta$ is the fraction of total aldehydes which are not formaldehyde. Both parameters can be specified with a high degree of confidence.

Consider the O-$HC_1$ reaction for propylene and 2-butene which, respectively, contain external and internal double bonds.



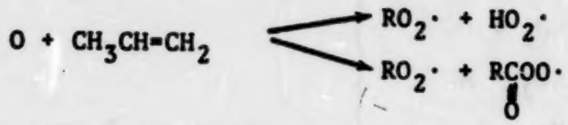
$$O + CH_3CH{=}CH_2 \rightarrow |CH_3CH_2\overset{}{\underset{O}{\underset{\|}{C}}}H^*| \rightarrow CH_3CH_2\cdot + \dot{C}HO$$

$$O + CH_3CH{=}CH_2 \rightarrow |CH_3\underset{O}{\underset{\|}{C}}CH_3^*| \rightarrow CH_3\underset{O}{\underset{\|}{C}}\cdot + \dot{C}H_3$$



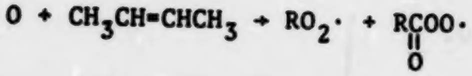
$$O + CH_3CH{=}CHCH_3 \longrightarrow \left[CH_3\underset{\overset{\|}{O}}{C}CH_2CH_3\right]^{*} \longrightarrow CH_3\underset{\overset{\|}{O}}{\dot{C}} + CH_3\dot{C}H_2$$

If we now assume that alkyl and acyl radicals react rapidly with $O_2$ and that $\dot{C}HO$ decomposes into $CO + HO_2$ in the presence of $O_2$, these reactions can be rewritten in our generalized notation as



$$O + CH_3CH{=}CH_2 \begin{array}{l} \nearrow RO_2\cdot + HO_2\cdot \\ \searrow RO_2\cdot + R\underset{\overset{\|}{O}}{C}OO\cdot \end{array}$$

and



$$O + CH_3CH{=}CHCH_3 \rightarrow RO_2\cdot + R\underset{\overset{\|}{O}}{C}OO\cdot$$

Now, if we further assume that O will react with equal probability with either carbon attached to the double bond, $\alpha = ½$ for propylene and $\alpha = 1$ for 2-butene. By the same reasoning $\alpha$ can be shown to be zero for ethylene.

During smog chamber studies of the propylene-$NO_x$ system, equal quantities of formaldehyde and higher aldehydes are observed to form. $\beta$ is thus equal to ½. In the case of toluene, Altshuller et al. (1970)have observed that only 15% of the aldehydes are formaldehyde. In this case $\beta$ is equal to 0.85.

In Table 4, we summarize the full mechanism proposed, an assemblage of all the inorganic, hydrocarbon, and free radical reactions into a generalized lumped mechanism. Note that the reactions of the inorganic species and the radical species, ROO·, $R\overset{\|}{C}OO\cdot$, and RO· , have already been outlined in previous sections.

## TABLE 4.

### A Lumped Kinetic Mechanism for Photochemical Smog

| | |
|---|---|
| $NO_2 + h\nu \xrightarrow{1} NO + O$ | The $NO_2$-$NO$-$O_3$ Cycle |
| $O + O_2 + M \xrightarrow{2} O_3 + M$ | |
| $O_3 + NO \xrightarrow{3} NO_2 + O_2$ | |
| $O + NO + M \xrightarrow{4} NO_2 + M$ | Important Reactions of O with Inorganic Species |
| $O + NO_2 \xrightarrow{5} NO + O_2$ | |
| $O + NO_2 + M \xrightarrow{6} NO_3 + M$ | |
| $O_3 + NO_2 \xrightarrow{7} NO_3 + O_2$ | The Chemistry of $NO_3$, $N_2O_5$, and $HNO_3$ |
| $NO_3 + NO \xrightarrow{8} 2NO_2$ | |
| $NO_3 + NO_2 \xrightarrow{9} N_2O_5$ | |
| $N_2O_5 \xrightarrow{10} NO_2 + NO_3$ | |
| $N_2O_5 + H_2O \xrightarrow{11} 2HNO_3$ | |
| $NO + HNO_3 \xrightarrow{12} HNO_2 + NO_2$ | Reactions of $HNO_3$ with Inorganic Species |
| $HNO_2 + HNO_3 \xrightarrow{13} H_2O + 2NO_2$ | |
| $NO + NO_2 + H_2O \xrightarrow{14} 2HNO_2$ | Chemistry of $HNO_2$ |
| $2HNO_2 \xrightarrow{15} NO + NO_2 + H_2O$ | |
| $HNO_2 + h\nu \xrightarrow{16} OH + NO$ | |
| $OH + NO_2 \xrightarrow{17} HNO_3$ | Important Reactions of OH with Inorganic Species |
| $OH + NO + M \xrightarrow{18} HNO_2 + M$ | |
| $OH + CO + (O_2) \xrightarrow{19} CO_2 + HO_2$ | |
| $HO_2 + NO \xrightarrow{20} OH + NO_2$ | Oxidation of NO by $HO_2$ |

TABLE 4. (Continued) A Lumped Kinetic Mechanism for Photochemical Smog

$$\left. H_2O_2 + h\nu \xrightarrow{21} 2OH \right\}$$

Photolysis of $H_2O_2$

$$\left.\begin{array}{l}
HC_1 + O \xrightarrow{22} ROO + \alpha R\overset{O}{\overset{\|}{C}}OO + (1 - \alpha)HO_2 \\
HC_1 + O_3 \xrightarrow{23} R\overset{O}{\overset{\|}{C}}OO + RO + HC_4 \\
HC_1 + OH \xrightarrow{24} ROO + HC_4 \\
HC_2 + O \xrightarrow{25} ROO + OH \\
HC_2 + OH \xrightarrow{26} ROO + H_2O \\
HC_3 + O \xrightarrow{27} ROO + OH \\
HC_3 + OH \xrightarrow{28} ROO + H_2O \\
HC_4 + h\nu \xrightarrow{29} \beta ROO + (2 - \beta)\, HO_2 \\
HC_4 + OH \xrightarrow{30} \beta R\overset{O}{\overset{\|}{C}}OO + (1 - \beta)\, HO_2 + H_2O
\end{array}\right\}$$

Hydrocarbon Oxidation Reactions

$$\left.\begin{array}{l}
ROO + NO \xrightarrow{31} RO + NO_2 \\
R\overset{O}{\overset{\|}{C}}OO + NO + (O_2) \xrightarrow{32} ROO + NO_2 + CO_2 \\
R\overset{O}{\overset{\|}{C}}OO + NO_2 \xrightarrow{33} R\overset{O}{\overset{\|}{C}}OONO_2 \\
RO + O_2 \xrightarrow{34} HO_2 + HC_4 \\
RO + NO_2 \xrightarrow{35} RONO_2 \\
RO + NO \xrightarrow{36} RONO
\end{array}\right\}$$

Reactions of Organic Free Radicals with NO, $NO_2$, and $O_2$

$$\left.\begin{array}{l}
HO_2 + HO_2 \xrightarrow{37} H_2O_2 + O_2 \\
HO_2 + ROO \xrightarrow{38} ROOH + O_2 \\
2ROO \xrightarrow{39} ROOR + O_2
\end{array}\right\}$$

Peroxy Radical Recombination Reactions

Given the mechanism shown in Table 4, we can now examine the assumptions inherent in the HS and EM mechanisms of Table 1. Both the HS and EM mechanisms have provisions for two lumped hydrocarbon species, usually specified to be of "high" and "low" reactivity. In each all the peroxy radicals are combined into the single species $RO_2$.

The main result of the reaction of atomic oxygen with lumped species is the formation of peroxy radicals, represented by

$$HC + O \rightarrow \alpha RO_2\cdot$$

Notice that production of hydroxyl radicals from O atom reactions with paraffins and aromatics has been neglected in this step.

The ozone-hydrocarbon reactions are assumed to yield peroxy radicals and aldehydes,

$$O_3 + HC \rightarrow \gamma RO_2\cdot + \gamma' RCHO$$

In the new mechanism it is assumed that a peroxyacyl and an alkoxyl radical, rather than the peroxyalkyl radical, form.

The OH-hydrocarbon reactions are assumed to yield peroxy radicals and a small quantity of aldehydes,

$$HC + OH\cdot \rightarrow \beta RO_2\cdot + \beta' RCHO$$

The remaining organic reactions are

$RO_2\cdot + NO \rightarrow NO_2 + \varepsilon OH\cdot$

$RO_2 + NO_2 \rightarrow PAN$

By comparison of the first reaction with the more correct reactions,

$ROO\cdot + NO \rightarrow NO_2 + \varepsilon OH\cdot + (1 - \varepsilon) RO\cdot$

$RCOO\cdot + NO \rightarrow NO_2 + ROO\cdot$

we see that regeneration of ROO· has been neglected in the conversion of NO to $NO_2$ by peroxyalkyl and peroxyacyl radicals. Thus, the $\varepsilon$ in the HS and EM mechanisms cannot be interpreted as the fraction of $RO_2\cdot$ that is $HO_2\cdot$ as it is in the more correct reactions, but rather only as an empirical parameter. As a result, the original stoichiometric coefficients $\alpha$, $\beta$ and $\gamma$ cannot be assigned the actual values that would be expected from the chemistry of the individual species. Rather, the $\alpha$, $\beta$, $\gamma$ and $\varepsilon$ become a set of parameters governing the chain length (the average number of free radical reactions, or propagation steps, that occur as a result of each initiation reaction). This lack of direct correspondence of the generalized stoichiometric coefficients in the HS and EM mechanisms to actual stoichiometric coefficients is the chief weakness of the two mechanisms. By virtue of its increased detail, the new lumped mechanism of Table 4 circumvents this shortcoming, as the stoichiometries are derivable directly from the underlying chemistry of each elementary reaction.

The generalized coefficients $\beta$ and $\epsilon$ in the HS mechanism play a role in simulating the effect of CO. It has been observed experimentally that CO concentrations of the order of 100 ppm or more accelerate the conversion of NO to $NO_2$ and the consumption of hydrocarbons when compared to similar experiments carried out in the absence of CO. Since OH· attacks both HC and CO and since the products of both reactions are radical species capable of oxidizing NO to $NO_2$ ($RO_2$· in the former case and $HO_2$· in the latter), in order for the addition of CO to a system to result in an *increase* in the rate of conversion of NO to $NO_2$, it is necessary that the number of NO molecules oxidized as a result of the CO-OH· reaction (always equal to one) be greater than the number of NO molecules oxidized as a result of the HC-OH· reaction. If more than one NO molecule is oxidized (on the average) to $NO_2$ as a result of chains initiated by the HC-OH· reaction, then the addition of CO to the system would effectively result in CO *inhibiting* the rate of oxidation of NO to $NO_2$. This effect would be attributable to the scavenging of OH· available for possible reaction with HC, an overall reaction capable of oxidizing more NO molecules than the single $HO_2$· produced in the CO-OH reaction. This is an apparent inconsistency, since, as we have noted, *experimentally* CO has been observed to *accelerate* the conversion of NO to $NO_2$. In Part III we propose a possible explanation for this effect.

## E. The Validation of Mechanisms With Smog Chamber Data

The validation of a mechanism using smog chamber data consists of four basic steps:

1. Estimation of Parameters. Estimate all unspecified parameters in the mechanism by comparison of the predicted concentration-time profiles with experimental data.

Estimation of lumped rate constants and stoichiometric coefficients can be carried out on a digital computer using either automatic parameter estimation routines or by trial and error. Of these two alternatives, by far the automatic parameter estimation is clearly preferable.

2. Determination of Confidence Regions. Using the predictions of the fitted model and the corresponding experimental data, determine the confidence limits associated with the estimated parameters. The level of uncertainty is a function of the model as well as of the data. A large confidence region indicates a high level of uncertainty in the joint parameter estimates, while an elongated region suggests that variations in the magnitude of the parameters have little effect on the model predictions.
3. Validation and Exercise of Mechanism. Employing the parameter estimates determined above, compute the predictions of the mechanism corresponding to available experiments over a range of initial conditions and, if possible, light intensities. Compare predictions with experimental observation, the experiments should clearly be *different* than those used to determine the parameters, and, if possible, should include conditions extrapolated beyond those of the experiments used to estimate the parameters.
4. Sensitivity Analysis. Perform a sensitivity analysis of the mechanism for the conditions in step 3. Vary each parameter over its expected range of values to determine the effect of these variations on the predicted concentration-time profiles. Compare the range of possible predictions with the data, taking careful account of the level of accuracy of the data.

In this section we shall consider briefly each of these aspects of validation. The objective is to set forth a consistent strategy for the validation of all present and potential mechanisms using modern techniques of parameter estimation and statistical analysis.

## 1. Estimation of Parameters in Reaction Rate Equations From Experimental Data

During the past 10 years powerful algorithms for estimating parameters in sets of coupled nonlinear ordinary differential equations have been developed (for example, see Bard and Lapidus (1968)). In this section we shall briefly review some of the key aspects of the estimation of parameters in reaction rate equations.

The problem can essentially be defined as follows. We have a set of N reaction rate equations of the form

$$\frac{dc_i}{dt} = f_i(c_1,\ldots,c_N,\ k_1,\ldots,k_p) \quad i = 1,2,\ldots N$$

$$c_i(0) = c_{i_o}$$

which contain $p$ unknown parameters $k_1,\ldots,k_p$ . Those parameters which are known are not explicitly indicated in $f_i$ . In addition, we have a set of $M$ experimental concentration measurements $y_i(t_r)$, $i = 1,2,\ldots,M_j$ $r = 1,2,\ldots,R$ where $M \leq N$ (not all dependent variables need be measured) and $R$ is the number of times at which data have been taken. These measurements are related to the concentrations in the model by

$$y_i(t_r) = c_i(t_r) + \text{(measurement errors)}, \quad i = 1,2,\ldots,M$$

where the first M concentrations are those that are measured. The so-called output error methods are those in which the k's are determined such that the sum of squares of the errors between the data and the predictions of the model,

$$\sum_{r=1}^{R} \sum_{i=1}^{M} [y_i(t_r) - c_i(t_r)]^2$$

is minimized. These methods assume that the only source of discrepancy between model and data are the experimental errors, i.e. that the model is correct. Examples of output error parameter estimation methods are given in Himmelblau (1971).

The principal disadvantage of output error methods is that they do not provide for uncertainty in the model (the mechanism) itself. Model errors may cause problems in achieving convergence of the iterative procedure that are the core of the output error methods or may produce parameter estimates that have inflated variances or uncertainties. However, as long as these methods are applied in situations where the possibility of an incorrect mechanism is small, they work quite well. It should be noted that output error methods normally require specification of weights of the output when more than one concentration is being measured.

A general method which avoids the problems inherent in the output error methods and has been successfully applied to a variety of real data is the maximum likelihood method (MLM). The MLM as developed by Mehra (1970) is comprised of three parts: (1) correction of measured concentrations for measurement error using Kalman filtering, (2) estimation of parameters in the mechanism using a modified Newton-Raphson optimization procedure (Lee, 1968), and (3) estimation of measures of model and measurement error.

### 2. Analysis of the Accuracy of Parameters Estimated in Rate Equations from Experimental Data

The second step in the validation of a kinetic mechanism is the analysis of the accuracy of the parameter estimates obtained in the first step. We assume that the model used is adequate to represent the data. If it is not, the parameter estimates will contain inaccuracies due, not only to the errors in the data, but also to the errors in the model. Thus, the procedures involved in this second step are designed to determine the inaccuracies in parameter estimates due only to errors in the data (under the assumption that the model is correct).

A measure of the precision of an estimated value is its estimated standard deviation. The standard deviation of a parameter estimate can be interpreted as follows. If we perform a large number of replicate experiments, each time estimating the same parameter, we can consider the estimate as a random variable since the data from which it has been estimated contain random errors. The standard deviation of the parameter estimate is a measure of its variation about the mean of the repeated determinations. Based on the standard deviation we can specify the *confidence limits* on the parameter estimate. For example, the 95% confidence limits are those two values of the parameter estimate between which we would expect the true value to lie with 95% probability.

In most parameter estimation procedures an estimate of the parameter standard deviation is obtained along with the parameter estimates themselves. The estimates of the standard deviations of individual parameters depend on (1) the data, (2) the data record length, and (3) the initial conditions. Analyses involving determination of standard deviations alone are concerned with only one parameter. Joint measures of uncertainty (confidence regions) are required in multi-parameter analyses. An excellent discussion of the determination of confidence intervals for parameters estimated in ordinary differential equations is given by Rosenbrock and Storey (1966).

The relationship between parameter estimation and the specification of confidence regions may be illustrated pictorally. Consider as an example the one-dimensional parameter estimation problem shown in Figure 3, in which the error criterion J is plotted against the value of the parameter estimate for two cases: (1) curve A, a "good" experiment, and (2) curve B, a "poor" experiment.*

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* "Good" is used in the sense of rich in information content, "poor" in the sense of low in information content.

The two curves shown might arise from choices of different initial conditions for the smog chamber reactants. The best estimates, $\hat{k}_A$ and $\hat{k}_B$, are those at the respective minima of the error criterion $J$. In a one-dimensional example, the curvature of $J$ in the vicinity of the minimum is related to the confidence (or degree of certainty) with which the parameter can be estimated. Because of the larger curvature of curve A, the true parameter value lies between points 1 and 2 with a higher probability than for the case of the "poor" experiment. This same notion of tighter confidence limits implying better parameter estimates carries over to the multi-dimensional parameter estimation problem. Illustrations of this case are given by Rosenbrock and Storey (1966).

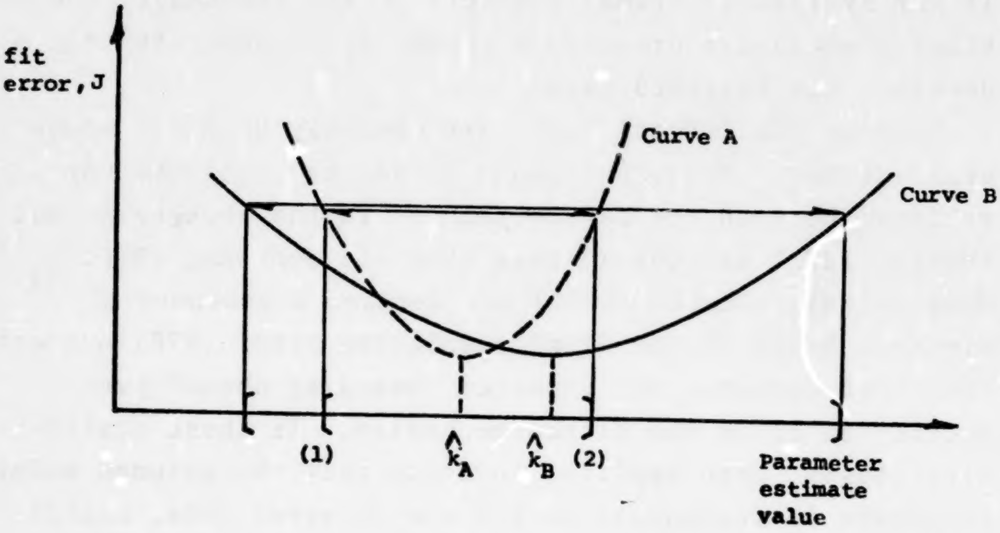

FIGURE 3. One-Dimensional Parameter Estimation Problem

### 3. Extrapolation of the Model to Data Other Than That Used to Estimate Parameters

A meaningful test of the accuracy of the parameter estimates is prediction. This is typically carried out by calculating concentration-time profiles from a set of data for which estimation has not been performed and comparing the predictions with the data. Thus, one reserves a few sets of data (not using them for estimation) for the purpose of verifying the accuracy of the parameter estimates obtained from the main body of data. The comparison between the predicted responses and the measured data is carried out primarily by examining the statistical properties of the residuals or fit errors. The model fit is deemed acceptable when the residuals are completely uncorrelated sample point to sample point. If any systematic trends are left in the residuals, the kinetic mechanism presumably is not fully adequate to describe the observed data.

Various statistical tests are commonly used for model verification. Principal among those that test the correlation between the sample points are the whiteness test (Mehra, 1971) and the $X^2$-test (Box and Jenkins, 1970). More recently Akaike (1970) has derived a goodness-of fit-test based on the final prediction error (FPE) criterion. This test computes the expected "one-step ahead" prediction error of the fitted mechanism. If these statistical tests, when applied, indicate that the assumed model structure is inadequate to fit the observed data, modifications to the model must be made.

### 4. Sensitivity Analysis

The final phase of the validation exercise is a sensitivity analysis. After establishing estimates for all parameters, the governing rate equations are integrated to obtain concentration-time profiles corresponding to a particular set of conditions (initial concentrations and light intensity). These concentration-time profiles constitute the so-called base case. Then, each of the parameters, the initial conditions, and the light intensity is systematically varied to ascertain the effect on the computed concentration-time behavior. The analog computer is particularly suitable for a sensitivity analysis since parameter variations can be effected by simply changing a potentiometer setting.

## F. Adaptation of Kinetic Mechanisms for Atmospheric Predictions

Up to this point we have confined our attention to the development and validation of a kinetic mechanism capable of simulating smog chamber reaction processes. The ultimate objective of developing such a mechanism is its use in atmospheric simulation studies. Therefore, once a mechanism capable of describing smog chamber experiments becomes available, we must consider its adaptation for use in the prediction of atmospheric reaction phenomena. In this section we shall outline those elements of atmospheric processes which may not receive recognition in a mechanism based solely on laboratory studies.

1. Kinetic mechanisms for photochemical smog previously formulated have not included $SO_2$ as a primary reactant. Both the lack of high $SO_2$ concentrations in the Los Angeles basin and a lack of understanding of the processes responsible for $SO_2$ oxidation in a photochemical oxidizing environment are responsible for its omission. However, there is clear evidence in Los Angeles, for example, that areas of the basin with the highest $SO_2$ concentrations frequently experience heavy haze formation. In addition, laboratory smog chamber experiments in which $SO_2$ is present in many cases have exhibited exceptionally high rates of aerosol formation. Clearly, there is a great need to include $SO_2$ as a primary reactant in photochemical kinetic mechanisms.
2. Somewhat related to the question of the role of $SO_2$ is the general area of *aerosol chemistry* in photochemical air pollution. Little is known at present about the actual mechanisms of formation of photochemical aerosols, although it is believed that aerosols may act primarily as sinks for gas phase reaction products rather than as catalysts for the gas phase reactions. No photochemical kinetic mechanisms available at this time include aerosol formation. In order to account properly for the effects of aerosols on observed gas phase concentrations and in order to predict rates of urban haze formation, it will be necessary to include reactions leading to aerosol formation in such kinetic mechanisms.
3. Many of the reported rate constants for atmospheric reactions have only been measured at 298°K. In many cases, such as for hydrocarbon oxidation reactions, there

is little information on activation energies, and thus on the *temperature dependence of the rate constants.* Obviously, application of a kinetic mechanism to atmospheric reactions requires knowledge of the temperature dependence of rate constants. Such dependence can easily be included in kinetic mechanisms; the difficulties lie, however, in the experimental measurement of values at different temperatures.

4. Most smog chamber experiments are conducted with a constant value of the radiation intensity. Hence, constant values for the first-order photodissociation rate constants, such as for $NO_2$, $HNO_2$, $H_2O_2$ etc., prevail. In the atmosphere, however, the *radiation intensity changes* naturally throughout the course of a day as well as when clouds appear and hazes are present. As with the temperature dependence of rate constants, changes in radiation intensity can be easily accounted for in a mechanism as long as the effect of the intensity changes on the dissociation rate constants is known. The difficulty arises in relating the actual radiation intensity at any time to the values of these dissociation rate constants. In an actual atmosphere, radiation intensity will vary with height above the ground due to the presence of aerosols which may scatter and absorb solar radiation. Ultimately, there must be included in full scale urban models a submodel which computes radiation intensity as a function of location and time in the presence of cloud cover and atmospheric aerosols.

5. Smog chamber experiments are generally carried out with well-defined initial hydrocarbon concentrations and compositions (except in auto exhaust irradiation experiments). In the atmosphere, however, the *hydrocarbon composition* is a function of time and location. Lumped reaction mechanisms, as we have seen, require classification of hydrocarbons into groups depending either on the hydrocarbon class or reactivity. Thus, the application of these mechanisms to the atmosphere will require knowledge of the spatial and temporal distribution of hydrocarbons, at least by class. The mechanisms, of course, must have the ability to treat such inhomogeneities. However, the key problem is that source inventories for hydrocarbon emissions and monitoring data generally report total hydrocarbons rather than a breakdown by class. The current lack of specific knowledge of atmospheric hydrocarbon distributions will hinder the application of lumped mechanisms to the atmosphere. In view of this lack of knowledge, the lumping employed in atmospheric studies may very well be different than that used for smog chamber studies.

There are two other phenomena which may be important in the atmosphere and not in a smog chamber. First, there may exist sinks for gas phase species. Potential sinks include aerosol particles, vegetation, and soil. Such sinks, while not altering the fundamental kinetics of the system, will have to be accounted for in an overall model. Second, the presence of turbulent concentration fluctuations will tend in some cases to cause the actual reaction rate to be different from the rate predicted on the basis of the mean concentrations. In order to account for the effect of turbulence on the observed reaction rates, it may be necessary to modify the kinetic equations so as to include the effect of turbulence within them. This point will be discussed in more detail in Sections III and VI.

Finally, we note that we have been discussing urban scale reaction phenomena. On a somewhat smaller scale there are two categories of source effluents that may have associated reaction phenomena quite different from that occurring on an urban scale:

1. *Plumes* - High local concentrations, temperatures and relative humidities may result in different reaction processes being important in plumes than in the more dilute urban basin; and
2. *Roadway Mixtures* - High fluxes of NO, CO and hydrocarbons, leading to elevated concentrations locally, may result in much higher reaction rates in the vicinity of the roadway than are normally expected in the regions of the airshed removed from the roadway. The extent to which these rapid reactions influence overall conversion rates in the atmosphere is not known.

## III. URBAN AIRSHED MODELS

Many difficult questions and complex issues arise in planning for the abatement and control of air pollution in an urban area. Certain key aspects of abatement planning are best addressed through the use of an urban airshed model; in some cases there are no alternative means of examining the critical issues. Included among those topics for which an airshed model may be particularly useful as an analytical tool are:

- the establishment of emissions control legislation,
- the evaluation of proposed emission control techniques and strategies,
- the planning of locations of future sources of air contaminants,
- planning for the control of air pollution incidents,
- the assessment of responsibility for existing levels of air pollution.

An airshed model is an essential component of planning studies in air pollution control because there commonly exists a need to establish a quantitative relationship between source emissions rates in an urban area and the magnitude of ground level contaminant concentrations that result from those emissions. Every urban locale has unique climatological and meteorological conditions. The spatial distribution of contaminant emissions, as well as the average composition of these emissions, varies from city to city. The concentration of secondary pollutants, formed in the atmosphere through the chemical reaction of primary (or emitted) pollutants, is influenced by local meteorology, emissions patterns, intensity of solar radiation, and many other variables. Clearly, in order to predict the spatial and temporal distributions of ground level concentrations of atmospheric contaminants, it is necessary to account for these many complexities through the simulation of the physical and chemical processes that actually give rise to the air quality observed - in short, through the use of an airshed model.

An airshed model may take many forms. It may be based on the equation(s) of conservation of mass for individual species, the equations of conservation of momentum, the equations of conservation of energy, or combinations of two or all three of these types of balances. Most commonly, however, as we shall discuss in this chapter, such models are based on the equations of conservation of mass. Models may describe the behavior of reactive species, or they may be limited in application to inert species. Furthermore, models may be formulated under the assumption of steady state behavior, or they may be descriptors of time-varying behavior. Temporal and spatial resolution of models may vary widely. Models may be based on a fixed grid, or they may be formulated so as to trace the variations in concentration in an "air parcel" moving with the average wind field.

Models based on the equations of continuity, of course, cannot predict variations in the velocity field (the momentum equations are needed) or the temperature field (the energy equations are needed). Wind and temperature information thus must be input as data. What such models can do, however, is relate in one equation (or set of equations, for more than one species) the effects of all the dynamic processes that influence the mass balance on a parcel of air. These include the transport, turbulent diffusion, and reaction of all pollutant species of interest. Also treated in such models are the introduction or removal of species.

A model based on the equations of conservation of mass requires, as a part of its formulation or as data input, information falling into the following categories: emissions, atmospheric chemistry, and meteorology. Emissions data includes information concerning emissions rates of all pollutants of interest from both fixed and mobile sources, often as a function of both location and time. Meteorological information needed as input includes wind speed, wind direction, mixing depth (or temperature as a function of elevation), and horizontal and vertical turbulent diffusivities, again usually as a function of location and time. A kinetic mechanism for atmospheric reactions is an essential component of a model that is capable of predicting concentrations of chemically reacting species, as is knowledge of reaction rate constants for the multiplicity of reactions that comprise the mechanism.

Once the model is properly formulated, and information concerning emissions, chemistry, and meteorology is appropriately incorporated, the model may be solved to obtain predicted concentrations of individual species as a function of location and time. Air quality data are normally required to assess the accuracy of the model, by comparing predictions with observations. Methods of solution may be simple or complex, involving small or large amounts of time. In the case of steady state models based on the conservation of mass for a single species, solutions may be read directly from charts or tables. For more complex formulations, numerical integration of the governing equations is usually necessary. Such solution procedures are commonly computer-based, often complex mathematically, and, in some cases, very time consuming.

In this chapter, we present a detailed discussion of urban airshed modeling. We first examine briefly the fundamental basis for models, so that we can, in a methodical manner, present the assumptions upon which commonly invoked approximations for the fundamental governing equations are based. We then discuss some of the more practical aspects of modeling, such as the implementation of models and the levels of uncertainty in the input variables. We then examine in some detail the relationship of the kinetic mechanism to the urban airshed model. Some specific questions that may be of interest to the reader that we address include the following:

1. What are the inherent limitations imposed on the spatial and temporal resolution employed in airshed models?
2. What levels of accuracy can be expected from airshed models in view of the uncertainties in input variables and the inherent limitations of the models themselves?
3. What fundamental restrictions, if any, are imposed on kinetic models that are to be included in airshed models?
4. What theoretical problems require further study in order to (a) better define the applicability and scope of current airshed models and (b) develop improved models?

Before proceeding, we wish to point out that the presentation which follows is a rather carefully constructed exposition of modeling. Our aim in writing it in this way is to provide a rigorous, unambiguous, concise development of the forms of airshed models that are commonly in use. A major consequence of adopting this approach, however, is that the presentation is largely mathematical, often involving relationships unfamiliar to the chemist. As a result, we make two recommendations to the reader. First, we suggest that on a first reading he not concern himself unduly with the mathematical arguments presented. Skimming the chapter should be sufficient. (We are aware, in fact, that many readers may not wish to confront the mathematics directly at any time, whether on a first or sixth reading.) Second, we would urge any reader who is seriously concerned with the role of chemical kinetics in airshed modeling, or with airshed modeling in general, or who will be working with such models, to carefully read the chapter (after skimming it initially) to gain an understanding of the basis of such models and of their uses, their shortcomings, and their limitations. It is to provide such an understanding that this chapter was included in this document.

## A. Fundamental Theory of Air Pollution Modeling

An urban air pollution model is, in essence, a description of the dynamic behavior of inert and reactive gaseous species in a turbulent flow. In this introductory section we discuss possible approaches to, and difficulties inherent in, properly describing the transport, turbulent diffusion, and reaction of gases in the atmosphere. In the section following we discuss the types of airshed models that have been developed to date, together with the assumptions underlying each. We include this and the following section because we believe that it is vital that individuals who develop or apply airshed models be clearly aware of the assumptions inherent in their derivation, and thus of the restrictions that limit their applicability.

In this section we shall develop the relationships for certain statistical properties of the concentrations of species in turbulence. These relationships will subsequently form the basis for the governing equations on which urban airshed models are based. The treatment in this section is divided into two parts, corresponding to the two fundamental ways of describing the behavior of species in turbulence. The first is the so-called *Eulerian* approach, in which the behavior of species is described relative to fixed coordinates (the most common way of describing concentration changes in a flowing system). The second is the so-called *Lagrangian* approach, in which concentration changes are described from the viewpoint of one traveling with the fluid. The two approaches yield different types of mathematical relationships for the pollutant concentrations. Each type of relationship is, of course, a valid description of turbulent diffusion; however, each has shortcomings which limit its applicability and which, of course, render exact description of the species concentrations impossible.

### 1. The Eulerian Approach

Consider N species in a fluid. The concentration of each species must, at any instant in time, satisfy a material balance taken over a volume element. Thus, any accumulation of material over time, when added to the net amount of material convected into the volume element, must be balanced by an equivalent amount of material that is produced by chemical reaction in the "element", that is emitted into it from sources, and that enters by molecular diffusion. Expressed mathematically, the concentration of each species $c_i$ must satisfy the continuity equation,

$$\frac{\partial c_i}{\partial t} + \sum_{\alpha=1}^{3} \frac{\partial}{\partial x_\alpha} (u_\alpha c_i) = \sum_{\alpha=1}^{3} D_i \frac{\partial^2 c_i}{\partial x_\alpha \partial x_\alpha} \qquad (1)$$

$$+ R_i(c_1,\ldots,c_N,T) + S_i(\underset{\sim}{x}, t)^*$$

$$i=1,2,\ldots,N$$

where

$u_\alpha$ = $\alpha^{th}$ component of the wind velocity, $\alpha = 1,2,3$
$D_i$ = molecular diffusivity of species $i$ in air, $i = 1,2,\ldots,N$
$R_i$ = rate of generation of species $i$ by chemical reaction
$T$ = fluid temperature
$S_i$ = rate of addition of species $i$ from volumetric source

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[*] $\underset{\sim}{x}$ represents the position vector in the system, $(x_1,x_2,x_3) \equiv (x,y,z)$ .

In addition to the requirement that the $c_i$ satisfy (1), the fluid velocities $u_\alpha$ and the temperature T must satisfy the Navier-Stokes and energy equations, respectively, which themselves are coupled through the $u_\alpha$ , $c_i$ and T with the total continuity equation and the ideal gas law. For many fluid systems it is necessary to carry out a simultaneous solution of the coupled equations of mass, momentum and energy conservation to account properly for the changes in T , $c_i$ and $u_\alpha$ and the effects of the changes of each of these on each other. In considering the behavior of contaminants in air, however, it is usually quite reasonable to assume that, since pollutants are, in general, present in the atmosphere at parts-per-million concentrations, the presence of pollutants in the atmosphere does not affect the meteorology to any detectable extent. Under this assumption, the equations of continuity for contaminant species can be solved independently of the coupled momentum and energy equations. Consequently, the fluid velocities $u_\alpha$ can be considered to be independent of the $c_i$ . There is, however, perhaps one important exception, one that is frequently observed in the Los Angeles area--the attenuation of incoming radiation by atmospheric contaminants that are present in high concentration. The temperature of the polluted layer may also be measurably altered due to its absorption, reflection and scattering of radiation. None of the models currently available include provisions for this coupling between pollutant concentrations, energy impact, and meteorology. Although in most cases we would expect these effects to be negligible, a lack of their consideration is a possible shortcoming of current models.

Since atmospheric flows are turbulent, it is conventional to replace $u_\alpha$ by the sum of a deterministic and a stochastic component, $\overline{u}_i + u_i'$ . Replacing $u_\alpha$ by $\overline{u}_\alpha + u_\alpha'$ in (1) gives*

$$\frac{\partial c_i}{\partial t} + \sum_{\alpha=1}^{3} \frac{\partial}{\partial x_\alpha} [(\overline{u}_\alpha + u_\alpha') c_i] = \sum_{\alpha=1}^{3} \frac{\partial^2 c_i}{\partial x_\alpha^2} \tag{2}$$

$$+ R_i(c_1,\ldots,c_N) + S_i(\underset{\sim}{x},t)$$

Since the $u_\alpha'$ are random variables, the $c_i$ resulting from the solution of (2) must also be random variables. Thus, the determination of the $c_i$ , in the sense of specifying a value of this variable at any time, is not possible; rather, we can at best derive the probability density functions satisfied by the $c_i$ . Unfortunately, the complete specification of the probability density function for a stochastic process as complex as atmospheric diffusion is almost never possible. Instead, we must be satisfied with the determination of the mean value, $\langle c_i(\underset{\sim}{x},t)\rangle$†, of the random concentrations. This mean value is interpreted as the average value of $c_i(\underset{\sim}{x},t)$ at location, $\underset{\sim}{x}$ , at time $t$ over a very large number of repetitions of the turbulent flow experiment. In the terminology of probability theory, such a mean value is called an *ensemble* mean. Clearly, an individual measurement may differ considerably from the mean $<c_i>$ . We represent the concentration $c_i$ as $<c_i> + c_i'$ , where the concentration fluctuation $c_i'$ has by definition a mean value of zero, $<c_i'> = 0$ .

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* We assume that the temperature is constant, and thus the dependence of $R_i$ on $T$ need not be explicitly indicated. It is not necessary to make this assumption; rather, it simplifies the presentation.

† We denote the mean value of the concentration by brackets, < >, and that of the velocities by overbars, since the process by which the average velocities are determined is ordinarily a *time* average rather than an *ensemble* average.

Substituting $c_i = <c_i> + c_i'$ into (2) and taking the mean value of the resulting equation yields

$$\frac{\partial <c_i>}{\partial t} + \sum_{\alpha=1}^{3} \{ \frac{\partial}{\partial x_\alpha} (\bar{u}_\alpha <c_\alpha>) + \frac{\partial}{\partial x_\alpha} <u_\alpha' c_i'> \} = D_i \sum_{\alpha=1}^{3} \frac{\partial^2 <c_i>}{\partial x_\alpha^2}$$

$$+ <R_i(<c_1> + c_1', \ldots, <c_N> + c_N')> + S_i(\underset{\sim}{x},t) \qquad (3)$$

Now, consider for the moment the simple case of an inert species, i.e. $R_i = 0$ . We note that (3) contains dependent variables $<c>$ and $<u_\alpha' c'>$, $\alpha=1,2,3$ . We thus have four dependent variables and only one equation. In order to provide a basis for solving this equation one might attempt to generate equations for the new dependent variables $<u_\alpha' c'>$, $\alpha=1,2,3$ . We can derive an equation for the $<u_\alpha' c'>$ by subtracting (3) from (2), leaving an equation for $c'$ , and then multiplying the resulting equation by $u_\alpha'$ and averaging over all terms. If this is done, the constructed equations take the form

$$\frac{\partial}{\partial t} \langle u_\alpha' c' \rangle + \sum_{\beta=1}^{3} \left\{ \frac{\partial}{\partial x_\beta} (\bar{u}_\beta \langle u_\alpha' c' \rangle) + \langle u_\alpha' u_\beta' \rangle \frac{\partial \langle c \rangle}{\partial x_\beta} \right\} =$$

$$\sum_{\beta=1}^{3} \frac{\partial}{\partial x_\beta} \left[ D \frac{\partial}{\partial x_\beta} \langle u_\alpha' c' \rangle - \langle u_\alpha' u_\beta' c' \rangle \right] \qquad \alpha=1,2,3 \tag{4}$$

While we have derived the desired equations, we have at the same time introduced six new dependent variables $\langle u_\alpha' u_\beta' c' \rangle$, $\alpha,\beta = 1,2,3$. If we generate additional equations for these variables, we find that still more dependent variables appear in these equations. This problem, arising in the Eulerian description of turbulent diffusion, is called the *closure problem*, a problem for which no general solution has yet been found.

The problem of closure becomes more severe if a nonlinear chemical reaction is occurring. Consider, for example, the decay of the single species by a second order reaction. Then the term $\langle R_i \rangle$ in (3) becomes $-k_2(\langle c \rangle^2 + \langle c'^2 \rangle)$, where $\langle c'^2 \rangle$ is a new dependent variable. If we were to write an equation for $\langle c'^2 \rangle$, additional new dependent variables, $\langle u_\alpha' c'^2 \rangle$, $\langle c'^3 \rangle$ and $\langle (\partial c'/\partial x_\beta)(\partial c'/\partial x_\beta) \rangle$ are introduced.

In summary, in order to use Eulerian equations of the type (3) to compute mean concentrations of air pollutants, we must overcome the closure problem by assuming some relationship between the dependent variables of higher order and those of lower order. Shortly we shall discuss conventional means of closing equation (3).

## 2. The Lagrangian Approach

The Lagrangian approach to studying the behavior of species in turbulence is based on considering the statistics of a single representative fluid particle in the flow. The fundamental quantity which embodies all the information on the statistics of a fluid particle is the transition probability density:

$Q(\underset{\sim}{x},t|\underset{\sim}{x}',t')$ = the probability that if a single "marked" fluid particle is at $\underset{\sim}{x}'$ at time $t'$, it will undergo a displacement to $\underset{\sim}{x}$ at time $t$.

Although Q refers to a single fluid particle, it can also describe the displacements of a "swarm" of fluid particles, or a continuous distribution of solute in a turbulent fluid, since the statistical behavior of a single particle is derived in principle from that of a very large number of identical particles.

The mean concentration of a solute at any location $\underset{\sim}{x}$ and time t can be related to that at an earlier time to by the following general relation (Monin and Yaglom, 1971)

$$\langle c(\underset{\sim}{x},t)\rangle = \int_{-\infty}^{\infty} Q(\underset{\sim}{x},t|\underset{\sim}{x}_0,t_0)\langle c(\underset{\sim}{x}_0,t_0)\rangle \, d\underset{\sim}{x}_0 \qquad (5)$$

If, in addition to the material present at $t_0$, there are continuous sources of the species (solute) in the fluid injected at the rate $S(\underset{\sim}{x},t)$, (5) becomes

$$\langle c(\underset{\sim}{x},t)\rangle = \int_{-\infty}^{\infty} Q(\underset{\sim}{x},t|\underset{\sim}{x}_o,t_o)\,\langle c(\underset{\sim}{x}_o,t_o)\rangle\, d\underset{\sim}{x}_o + \int_{t_o}^{t}\int_{-\infty}^{\infty} Q(\underset{\sim}{x},t|\underset{\sim}{x}',t')\, S(\underset{\sim}{x}',t)\, d\underset{\sim}{x}'dt' \tag{6}$$

This is the fundamental relation for the mean concentration of a species in a turbulent flow in which there are sources. The determination of $\langle c(\underset{\sim}{x},t)\rangle$ given the initial concentration distribution $\langle c(\underset{\sim}{x}_o,t_o)\rangle$ and the sources, $S(\underset{\sim}{x}',t')$, rests on the evaluation of the transition density $Q(\underset{\sim}{x},t|\underset{\sim}{x}',t')$. In contrast to the Eulerian approach, no closure problem arises here. Instead, we need to know the probability that a particle released into the flow can be found at any particular location at any designated subsequent time. Unfortunately, such a thorough knowledge of the properties of a turbulent field is unavailable except in the simplest of circumstances. Also, there is no convenient way to include nonlinear chemical reactions in the Lagrangian formulation, since one would have to keep track of all possible particle "collisions". Nevertheless, under certain conditions (to be specified later) it is possible to use a modified form of (6) as the basis for a model in which nonlinear chemical reactions are admissible.

## 3. Summary

The techniques for describing the statistical properties of the concentrations of tagged particles, such as air pollutants, in a turbulent fluid can be divided into two broad catagories--*Eulerian* and *Lagrangian*. The Eulerian methods attempt to formulate the concentration statistics in terms of the statistical properties of the Eulerian fluid velocities, i.e. the velocities measured at fixed points in the fluid. A formulation of this type is very useful in air pollution modeling, not only because the Eulerian statistics are readily measurable*, but also because the mathematical expressions are directly applicable in situations in which chemical reactions are taking place. Unfortunately, the Eulerian approaches lead to a serious mathematical obstacle known as the closure problem, for which no generally valid solution has yet been found. A number of approximate solutions have been proposed (see Section B) but each leads to an equation which gives accurate results for only a limited class of problems.

By contrast, the Lagrangian techniques attempt to describe the concentration statistics in terms of the statistical properties of the displacements of groups of particles released in the fluid. The mathematics of this approach are more tractable than that of the Eulerian method in that no closure problem is encountered, but the applicability of the resulting equations is limited due to the difficulty of accurately determining the required particle statistics. Moreover, the equations are not directly applicable to problems involving nonlinear chemical reactions.

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* As determined from continuous time recordings of the wind velocities monitored by a fixed network of anenometers.

In the preceding sections we demonstrated that exact solution for the mean concentrations $\langle c_i(\underset{\sim}{x},t)\rangle$ of even an inert species in a turbulent fluid is not in general, possible using either the Eulerian or Lagrangian approaches. We must now consider what additional assumptions and approximations can be invoked to derive the equations upon which practical urban airshed models may be based. In the section to follow we will proceed from the two basic equations for $\langle c_i(x,t)\rangle$, namely (3) and (6), to obtain mathematical formulations for the urban airshed models that are currently in use. A particularly important aspect of the next section will be delineation of the assumptions and limitations inherent to each model.

## B. Approaches to Obtaining Approximate Models

We have seen that both the Eulerian and Lagrangian approaches to the prediction of the behavior of species in turbulence lead to certain difficulties which render exact solution for the mean concentrations impossible. In this section we shall outline some of the more common approximations which are made in order to obtain useful models for the mean concentrations of reactive species in turbulence.

### 1. Eulerian Approaches

The objective of this subsection is to describe means for obtaining a closed form of (3). To do this we introduce relationships between the mean concentrations and the new dependent variables in (3), $\langle u_\alpha' c_i' \rangle$, $\alpha = 1,2,3$, as well as any that might arise from $\langle R_i \rangle$ if chemical reactions are taking place. For the moment let us consider only the case of chemically inert species, so that $R_i = 0$ .

The simplest means of relating the $\langle u'_\alpha c'_i \rangle$ to the $\langle c_i \rangle$ is by the mixing length assumption, i.e. that the turbulent mass flux $\langle u'_\alpha c'_i \rangle$ is linearly related to the gradients of $\langle c_i \rangle$ ,

$$\langle u'_\alpha c'_i \rangle = -\sum_{\beta=1}^{3} K_{\alpha\beta} \frac{\partial \langle c_i \rangle}{\partial x_\beta} \qquad \alpha = 1,2,3 \qquad (7)$$

where $K_{\alpha\beta}$ is the $(\alpha , \beta )$ element of a tensor $K$ and is called an *eddy diffusivity*. Since (7) is essentially only a definition of the $K_{\alpha\beta}$ , which are in general functions of location and time, we have, by means of (7), replaced the unknowns $\langle u'_\alpha c'_i \rangle$ with a new set of unknowns, $K_{\alpha\beta}$ , $\alpha$ , $\beta = 1,2,3$ .

In using (3) two other assumptions not related to the closure problems are ordinarily invoked, namely (1) that molecular diffusion is negligible when compared with turbulent diffusion and (2) that the atmosphere is incompressible. With reference to (3) this implies that

$$(1) \quad D_i \frac{\partial^2 \langle c_i \rangle}{\partial x_\alpha \partial x_\alpha} << \frac{\partial}{\partial x_\alpha} \langle u'_\alpha c'_i \rangle$$

and

$$(2) \quad \frac{\partial \bar{u}_\alpha}{\partial x_\alpha} = 0$$

With these assumptions and (7), (3), for inert pollutants, becomes

$$\frac{\partial\langle c_i\rangle}{\partial t}+\sum_{\alpha=1}^{3}\bar{u}_\alpha\frac{\partial\langle c_i\rangle}{\partial x_\alpha}=\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3}\frac{\partial}{\partial x_\alpha}\left(K_{\alpha\beta}\frac{\partial\langle c_i\rangle}{\partial x_\beta}\right)+S_i(\underset{\sim}{x},t) \quad (8)$$

where the $K_{\alpha\beta}$ are a function of location and time. If the coordinate axes coincide with the principal axes of the eddy diffusivity tensor $K$, only the three diagonal components of $K$ are non zero. Since there is no preferred horizontal direction we let these three components be $\{K_H, K_H \text{ and } K_V\}$. Equation (8) then reduces to a form reminiscent of the ordinary molecular diffusion equation,

$$\frac{\partial\langle c_i\rangle}{\partial t}+\sum_{\alpha=1}^{3}\bar{u}_\alpha\frac{\partial\langle c_i\rangle}{\partial x_\alpha}=\frac{\partial}{\partial x}\left(K_H\frac{\partial\langle c_i\rangle}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_H\frac{\partial\langle c_i\rangle}{\partial y}\right)$$
$$+\frac{\partial}{\partial z}\left(K_V\frac{\partial\langle c_i\rangle}{\partial z}\right)+S_i(x,y,z,t) \quad (9)$$

$$i = 1,2,\ldots N$$

This equation has been called by Monin and Yaglom (1971) the *semi-empirical equation of atmospheric diffusion.*

Let us now consider the case in which chemical reactions are occurring. We again direct the reader's attention to (3). In air pollution modeling studies involving chemical reactions it has been customary not only to employ the eddy diffusivity assumption as outlined above but also to replace $\langle R_i(\langle c_i\rangle + c_i, \ldots, \langle c_N\rangle + c_N')\rangle$ with $R_i(\langle c_i\rangle, \ldots, \langle c_N\rangle)$, thereby neglecting the effect of concentration fluctuations on the rate of reaction. The resulting equation is

$$\frac{\partial \langle c_i \rangle}{\partial t} + \sum_{\alpha=1}^{3} \bar{u}_\alpha \frac{\partial \langle c_i \rangle}{\partial x_\alpha} = \frac{\partial}{\partial x} \left(K_H \frac{\partial \langle c_i \rangle}{\partial x}\right) + \frac{\partial}{\partial y} \left(K_H \frac{\partial \langle c_i \rangle}{\partial y}\right)$$

$$+ \frac{\partial}{\partial z} \left(K_V \frac{\partial \langle c_i \rangle}{\partial z}\right) + R_i(\langle c_i \rangle, \ldots, \langle c_N \rangle) + S_i(\underset{\sim}{x}, t) \qquad (10)$$

Due to the assumptions:

(1) mixing length approximation to the turbulent mass fluxes, (7)

(2) neglect of concentration fluctuations

(10) is *not* the fundamental equation governing the mean concentrations of reactive substances in turbulence, but rather is only an approximate equation which is considerably limited in its applicability to reactive pollutants in the atmosphere.

Lamb (1973) has derived mathematical statements for the conditions under which (10) is a valid representation of atmospheric transport and chemical reaction. In brief, the conditions are:

(1) that the ratio of the Lagrangian time scale* of the turbulence to the time scale for chemical reactions be much less than one.

(2) that the ratio of the characteristic length scale of the concentration field (i.e. the source

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* The Lagrangian time scale of turbulence may be visualized as follows. Let us define a correlation coefficient between the fluid velocities at a point at two times $t_o$ and $t$ . The Lagrangian time scale is given by $(t_1 - t_o)$, the largest difference in times such that the correlation coefficient is no less than some preselected level.

distribution) to that of the turbulence be much greater than one, and

(3) that the ratio of the characteristic time scale for changes in concentration field to that for the turbulence be much greater than one.

In other words, (10) is a valid description of turbulent diffusion and chemical reaction as long as the reaction processes are slow compared to turbulent transport and the characteristic length and time scales for changes in the mean concentration field are large compared to the corresponding scale for turbulent transport.

Because the Lagrangian time scale $T_L$ and length scale $\langle u_\alpha'^2 \rangle^{1/2} T$ are often quite large in the atmosphere, these conditions are violated near strong isolated sources. For example, for the lateral turbulent velocity component, $T_L$ may be about 1 minute and $\langle u_2'^2 \rangle \approx 1$ meter/sec. Thus, to satisfy condition (2) above, the spatial scale for variations in $\langle c \rangle$, and hence $S$, must be the order of 500 meters, which is not the case in the vicinity of point and line sources. In addition, under these conditions the time scale of the fastest reactions must be no smaller than about 10 min. This condition is known to be violated near sources of NO in the presence of $O_3$.

The conclusion we draw at this point is that (10) is a valid model *provided it is applied under conditions in which chemical reactions are "slow" and the distribution of sources is fairly uniform.* These conditions can be met by spatially averaging source emissions and considering only the slower, rate-determining chemical reactions in the function $R_i$.

We have noted that in the commonly used equation (10), the contributions of concentration fluctuations $c_i'$ to the rate of reaction have been neglected. We have seen that this omission can be justified only if the reactions included take place on time scales much slower than the turbulent dispersion. However, the question of how to treat $<R_i>$ if these conditions are not met remains an often issue. We shall now discuss this problem briefly, as it is an important one for future study.

We would like to consider the possible role that concentration fluctuations may play in determining the rate of chemical reactions. To do so we consider the reaction $A + B \rightarrow C + D$ which proceeds at a rate $kc_A c_B$. The mean reaction rate in an infinitesimal volume of fluid is given by

$$\frac{d<c_A>}{dt} = -k<c_A c_B> = -k[<c_A><c_B> + <c_A' c_B'>] \qquad (11)$$

where the temperature has been assumed constant. The approximation of replacing $<R_i>$ by $R_i(<c_i>,\ldots,<c_N>)$ would correspond in this case to letting

$$\frac{d<c_A>}{dt} = -k<c_A><c_B> \qquad (12)$$

Clearly, this approximation is valid only if $<c_A' c_B'> << <c_A><c_B>$. From (11) we can see that if the correlation between $c_A'$ and $c_B'$ is positive, i.e. $<c_A' c_B'> > 0$, the actual reaction rate will be faster than that predicted by (12). On the other hand, if the reactants are randomly mixed or if positive fluctuations in one species are associated with negative fluctuations in the other, the reaction rate would be suppressed relative to the uniformly mixed case (12). Which of these two situations would prevail in a particular situation depends on the rate of mixing of the species by molecular and turbulent diffusion as compared to the rate of reaction. Thus, in order to assess the possible importance of terms of the form $<c'_A c'_B>$ it will be necessary to consider the other processes responsible for formation and destruction of the fluctuations, $c'_A$ and $c'_B$ .

We can derive a general conservation equation for the term $<c'_A c'_B>$ in the following way. The continuity equations for A and B are

$$\frac{\partial c_A}{\partial t} + \sum_{\alpha=1}^{3} u_\alpha \frac{\partial c_A}{\partial x_\alpha} = \sum_{\alpha=1}^{3} D \frac{\partial^2 c_A}{\partial x_\alpha^2} - k c_A c_B \tag{13}$$

$$\frac{\partial c_B}{\partial t} + \sum_{\partial=1}^{3} u_\alpha \frac{\partial c_B}{\partial x_\alpha} = \sum_{\alpha=1}^{3} D \frac{\partial^2 c_B}{\partial x_\alpha^2} - k c_A c_B \tag{14}$$

where we have assumed that $D_A = D_B = D$ . Letting $u_\alpha = \bar{u}_\alpha + u'_\alpha$ , $c_A = <c_A> + c'_A$ , $c_B = <c_B> + c'_B$ and taking mean values of each equation we obtain

$$\frac{\partial <c_A>}{\partial t} + \sum_{\alpha=1}^{3} \bar{u}_\alpha \frac{\partial <c_A>}{\partial x_\alpha} + \sum_{\alpha=1}^{3} <u'_\alpha \frac{\partial <c_A>}{\partial x_\alpha}> = D \sum_{\alpha=1}^{3} \frac{\partial^2 <c_A>}{\partial x_\alpha^2}$$

$$- k(<c_A><c_B> + <c'_A c'_B>) \tag{15}$$

A similar equation can be derived for $\langle c_B \rangle$. Subtracting (15) and its counterpart for $\langle c_B \rangle$ from (13) and (14) yields equations for $c'_A$ and $c'_B$, e.g.

$$\frac{\partial c'_A}{\partial t} + \sum_{\alpha=1}^{3} \left\{ \bar{u}_\alpha \frac{\partial c'_A}{\partial x_\alpha} + u'_\alpha \frac{\partial \langle c_A \rangle}{\partial x_\alpha} + u'_\alpha \frac{\partial c'_A}{\partial x_\alpha} - \left\langle u'_\alpha \frac{\partial c'_A}{\partial x_\alpha} \right\rangle \right\} =$$

$$D \sum_{\alpha=1}^{3} \frac{\partial^2 c'_A}{\partial x_\alpha^2} - k c'_A \langle c_B \rangle - k c'_B \langle c_A \rangle - k c'_A c'_B + k \langle c'_A c'_B \rangle \qquad (16)$$

Multiplying (16) by $c'_B$ and multiplying the corresponding equation for $c'_B$ by $c'_A$, adding and taking mean values yields the desired equation for $\langle c'_A c'_B \rangle$

$$\frac{\partial}{\partial t} \langle c'_A c'_B \rangle + \underset{\textcircled{1}}{\sum_{\alpha=1}^{3} \bar{u}_\alpha \frac{\partial}{\partial x_\alpha} \langle c'_A c'_B \rangle} = \sum_{\alpha=1}^{3} \left\{ \underset{\textcircled{2}}{- \langle u'_\alpha c'_B \rangle \frac{\partial \langle c_A \rangle}{\partial x_\alpha} - \langle u'_\alpha c'_A \rangle \frac{\partial \langle c_B \rangle}{\partial x_\alpha}} \right.$$

$$\left. + \frac{\partial}{\partial x_\alpha} \Big( \underset{\textcircled{3}}{D \frac{\partial}{\partial x_\alpha} \langle c'_A c'_B \rangle} - \underset{\textcircled{4}}{\langle u'_\alpha c'_A c'_B \rangle} \Big) - \underset{\textcircled{5}}{2D \left\langle \frac{\partial c'_A}{\partial x_\alpha} \frac{\partial c'_B}{\partial x_\alpha} \right\rangle} \right\} \qquad (17)$$

$$- k \langle c'_A c'_B \rangle (\langle c_A \rangle + \langle c_B \rangle) - \underset{\textcircled{6}}{k \langle c'_A c'^2_B \rangle} - k \langle c'^2_A c'_B \rangle - k \langle c'^2_B \rangle \langle c_A \rangle$$

$$- k \langle c'^2_A \rangle \langle c_B \rangle$$

The terms in (17) have the following physical significance:

① = Convection of $<c'_A c'_B>$ by the mean flow
② = Generation of $<c'_A c'_B>$ by the mean gradients of A and B
③ = Molecular diffusion of $<c'_A c'_B>$ (nondissipative)
④ = Transport of $<c'_A c'_B>$ by turbulent velocity fluctuations
⑤ = Dissipation of $<c'_A c'_B>$ by molecular diffusion
⑥ = Net destruction of $<c'_A c'_B>$ by chemical reaction

In order to assess the relative importance of these various processes we must examine the sizes of the various terms in (17). However, (17) is quite complicated, and, in any case, it is difficult to draw any general conclusions from such an analysis as to the major processes responsible for the dynamics of $<c'_A c'_B>$ . Therefore, for the purposes of illustration, let us consider only the processes of molecular dissipation and chemical reaction, thereby assuming that $\bar{u}_\alpha = 0$ and that gradients in the mean concentrations are zero. Thus, in this case

$$\frac{\partial}{\partial t} <c'_A c'_B> = \sum_{\alpha=1}^{3} \left\{ \frac{\partial}{\partial x_\alpha} <u'_\alpha c'_A c'_B> - 2D <\frac{\partial c'_A}{\partial x_\alpha} \frac{\partial c'_B}{\partial x_\alpha}> \right\} \tag{18}$$

$$- k(<c_A> + <c_B>) <c'_A c'_B> - k<c'_A c'^2_B> - k<c'^2_A c'_B>$$

$$- k<c'^2_B><c_A> - k<c'^2_A><c_B>$$

In a formulation such as this, it is customary to represent the second term on the right hand side by a concentration microscale, as follows (Hinze, 1959):

$$2D < \frac{\partial c'_A}{\partial x_\alpha} \frac{\partial c'_B}{\partial x_\alpha} > = \frac{2D<c'_A c'_B>}{\lambda^2} , \qquad (19)$$

where $\lambda$ is a measure of the size of concentration eddies. Donaldson and Hilst (1972a) have estimated a typical value of $\lambda$ in the atmosphere to be 10 cm.

We would now like to compare the rate of dissipation of $<c'_A c'_B>$ by molecular diffusion, i.e. (19), to that by chemical reaction. From (19) we see that a characteristic time for decay of $<c'_A c'_B>$ by molecular diffusion is

$$\tau_{diff} = \frac{\lambda^2}{2D} \qquad (20)$$

A characteristic time for decay of $<c'_A c'_B>$ by chemical reaction is estimated from the term $-k(<c_A> + <c_B>)<c'_A c'_B>$ , and is taken to be

$$\tau_{chem} = [k(<c_A> + <c_B>)]^{-1} \qquad (21)$$

Let us now consider the relationship between the two characteristic times, $\tau_{diff}$ and $\tau_{chem}$ . If $\tau_{diff} <<$ $\tau_{chem}$ , the molecular dissipation of fluctuations will be the dominant contribution to the change of $<c'_A c'_B>$ in a volume element. In that case, diffusion will tend to smear out the fluctuations such that $\langle c_A' c_B' \rangle$ is always close to zero. Conversely, if $\tau_{diff} \gg \tau_{chem}$, i.e. very fast reactions, the decay of fluctuations due to the chemistry will predominate and $\langle c_A' c_B' \rangle$ will always tend to be approximately equal to $-\langle c_A \rangle \langle c_B \rangle$. In this case, A and B will be poorly mixed because the molecular dissipation of fluctuations is too slow to eliminate inhomogeneities. Then, the rate of disappearance of A and B by chemical reaction will be governed by the rate of molecular diffusion.

As a measure of the relative importance of diffusion and reaction, Donaldson and Hilst (1972b) have proposed that the ratio

$$\Gamma = \frac{\tau_{diff}}{\tau_{chem}} = \frac{\lambda^2 k}{2D} (\langle c_A \rangle + \langle c_B \rangle)$$

be computed for typical atmospheric reactions. If:

$$\Gamma \ll 1 \qquad \text{then} \qquad \langle c_A' c_B' \rangle / \langle c_A \rangle \langle c_B \rangle \approx 0$$

or

$$\Gamma \gg 1 \qquad \text{then} \qquad \langle c_A' c_B' \rangle / \langle c_A \rangle \langle c_B \rangle \approx -1$$

Assuming $\lambda = 10$ cm., Donaldson and Hilst (1972b) have calculated the value of $\Gamma$ for a number of individual atmospheric chemical reactions. For many reactions they found $\Gamma$ to be the order of $10^2$, suggesting that the fluctuating quantities might be important in determining the overall rate of such reactions. We can only view these results as qualitative indications of possible effects, because only individual isolated reactions were considered, rather than coupled sets of reactions such as actually occur in the atmosphere. In addition, the effect of turbulent mixing was not included in the above analysis.

Theoretical studies of closure methods for terms of the form $< c'_A c'_B >$, $< c'^2_A c'_B >$ , etc. have been the subject of several papers by Corrsin (1958) and O'Brien (1966, 1968a, 1968b, 1969, 1970, 1971, 1972). Additional theoretical work on chemical reactions in turbulence has been presented by Lee (1966) and Chung (1970). Experimental measurements of second order reactions in turbulent have been reported by Keeler et al. (1965) and Vassilatos and Toor (1965). Those studies provide a strong foundation for future work in analyzing the coupling of turbulence and chemical reactions.

*In summary, inhomogeneities in a reacting atmospheric mixture are capable of exerting significant effects on the overall reaction rate.* These inhomogeneities are currently not accounted for in large scale urban airshed models in which the rates of chemical reactions are taken to depend on the mean concentrations only. The effects may be important in the vicinity of major sources where high concentrations and inhomogeneous mixing may results in reaction rates different than those predicted on the basis of mean concentrations alone. This observation points to a need for studies of pollutant behavior in the vicinity of major sources.

## 2. Lagrangian Approaches

As we have seen, the utility of (6) rests on one's ability to evaluate the transition probability density $Q(\underset{\sim}{x},t|\underset{\sim}{x}',t')$. The question immediately arises: Are there any circumstances under which the form of $Q$ is known? If the turbulence is stationary and homogeneous, $Q(\underset{\sim}{x},t|\underset{\sim}{x}',t') = Q(\underset{\sim}{x} - \underset{\sim}{x}'; t - t')$, i.e. the transition density depends only on displacements in time and space and not on where or when the particle was introduced into the flow, and $Q$ is Gaussian (Monin and Yaglom, 1971).

The Gaussian density, coupled with (6), gives the well-known set of so-called Gaussian plume formulas (Slade, 1968; Turner, 1969) - normally applied with no decay of pollutant. These formulas are the classical relations for diffusion in stationary, homogeneous turbulence and have been used extensively in predicting pollutant dispersion from point and line sources. In particular, a fair degree of success has been achieved in predicting long-time averages of concentrations near the source ($x_i - x_{i_o} < 10$ km.) under steady meteorological conditions, when empirically determined values of the variances of the distribution [such as the Pasquill curves (Pasquill, 1962)] have been used. However, when so applied, the plume formulas must be regarded as empirical expressions capable of accurate prediction only for conditions that are reasonably similar to those under which the empirical variances were determined. However, due to the assumptions of stationary and homogeneous turbulence, which almost never prevail in atmospheric situations of interest, these equations are now recognized to be an inadequate basis for a general urban air pollution model.

Thus, we return to the problem of determining $Q(\underset{\sim}{x},t|\underset{\sim}{x}',t)$ in the nonstationary, inhomogeneous turbulence of the atmospheric surface layer. Perhaps the only feasible way of doing this is by numerical simulation of the turbulence, in a manner such as has been reported by Lamb (1971a) who used the fluid simulation model of Deardorff (1970). Because of the large computing requirements of such a simulation model, this approach does not appear to provide a practical basis for a full urban airshed model. In addition, there is presently no way in which nonlinear chemical reactions may be included within the framework of (6). We therefore conclude that (6) can be used as the basis of a general urban airshed model only for inert pollutants (or those that decay by a first-order reaction) and only when $Q$ can be determined from experimental data or numerical simulation. For an illustration of the use of such a model for CO in Los Angeles, we refer the reader to Lamb and Neiburger (1971).

## 3. Summary of Approximate Urban Airshed Models

In this section we have briefly discussed some conventional approximate equations for the mean concentrations of species in turbulence. In order to summarize the distinguishing features of the two general types of models, we list in Table 5 the assumptions employed in deriving their respective governing equations. Because there is no possibility of including in (6) nonlinear relationships expressing chemical kinetics, we shall henceforth focus on (10) as the basis for a generalized urban airshed model.

## C. Implementation of Urban Airshed Models

We have thus far limited our discussion to an examination of equations which might provide a suitable basis for a general urban airshed model. In this section we will focus almost entirely on (10) as the fundamental equation for such models. The remainder of Chapter III will be devoted to the *implementation* of the various types of urban airshed models which are more or less based on (10).

We divide the airshed models to be discussed into two basic categories:

- Grid Models
- Trajectory Models

In the grid model the airshed is divided into a three-dimensional grid, which can be envisioned as stacked layers of cells, each cell being perhaps one to two miles on a side and a few hundred feet high. The grid is then used as a basis for the numerical integration of the N coupled equations (10). In the trajectory approach a hypothetical column of air, which may or may not be well mixed vertically,

TABLE 5. Restrictions on the Applicability of Eulerian and Lagrangian Equations as the Basis for a General Urban Airshed Model

| | Parameter | Lagrangian Form (6) | Eulerian Form (10) |
|---|---|---|---|
| 1. | Coordinate system | none | Principal axes of $K_{\alpha\beta}$ |
| 2. | Source strength function | none | Spatial and temporal variations "smooth" compared to resolution of the equation |
| 3. | Initial condition distribution | none | Spatial variation "smooth" compared to resolution of the equation |
| 4. | Turbulence | none | Turbulent velocity fluctuations correlated on length and time scales much smaller than resolution of the equation |
| 5. | Mean velocity field $\overline{U}_i$ | none | Spatial and temporal variations "smooth" compared to resolution of the equation |
| 6. | Chemical reactions | first-order decay only | Time scales for the reactions slow compared to resolution of the equation |

is followed through the airshed as it is advected by the wind. Pollutants are emitted into the column, either at its base or as volume sources, and chemical reactions may take place within the column. Since these two classes of airshed models involve significantly different concepts in the implementation of (10) and therefore may have different requirements in terms of the treatment of atmospheric chemistry, it is important that each be examined in some detail.

### 1. Grid Models

As we have just noted, grid models refer to those in which (10) is solved numerically on a three-dimensional (in some cases, two-dimensional) grid, the specific form of the equation used being dependent on the simplifying assumptions made.

We begin by restating the basic model. In this way we can illustrate the means by which meteorological, chemical and source information enter into the formulation. The basic model consists of the N coupled (through the chemical reaction term $R_i(\langle c_1\rangle,\ldots,\langle c_N\rangle)$) partial differential equations:

$$\frac{\partial\langle c_i\rangle}{\partial t} + \sum_{\alpha=1}^{3} \bar{u}_\alpha \frac{\partial\langle c_i\rangle}{\partial x_\alpha} = \frac{\partial}{\partial x}\left(K_H \frac{\partial\langle c_i\rangle}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_H \frac{\partial\langle c_i\rangle}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_V \frac{\partial\langle c_i\rangle}{\partial z}\right) + R_i(\langle c_1\rangle,\ldots,\langle c_N\rangle) + S_i(\underline{x},t)$$

$$i = 1,2,\ldots N \qquad (10)$$

Meteorological information enters through:

1) the deterministic wind field, $\overline{u}_\alpha(x,y,z,t)$ , assumed to satisfy the overall continuity equation
2) the eddy diffusivities, $K_H(x,y,z,t)$ and $K_V(x,y,z,t)$
3) the dependence of $R_i$ on light intensity

Chemical information enters through $R_i(<c_1>,\ldots,<c_N>)$ , the rate of formation of species i in a chemical kinetic mechanism for reactions among the N species. Volume sources (those above ground) enter through $S_i(\underset{\sim}{x},t)$ .

The initial and boundary conditions associated with (10) incorporate further meteorological and source information. The initial condition is that $<c(\underset{\sim}{x},t_o)>$ is specified everywhere in the airshed. Vertical boundary conditions are:

$$-K_V \frac{\partial <c_i>}{\partial z} = Q_i(x,y,t) \qquad z = 0 \quad \text{(ground)}$$

and

$$\frac{\partial <c_i>}{\partial z} = 0 \qquad z = H(x,y,t) \text{ (top of polluted layer)}$$

where $Q_i(x,y,t)$ is the flux of species i from ground-level sources at location (x,y) and time t , and $H(x,y,t)$ is the height of the base of an elevated inversion (or a mixing height) at location (x,y) and time t . Horizontal boundary conditions specify concentration levels at points of flow into the airshed.

In discussing grid models we will examine a number of questions related to the practical implementation of the basic equations (10). First, we briefly describe the types of numerical methods which may be used for the solution of the N coupled partial differential equations comprising the model. We then discuss the effect of the spatial averaging inherent to carrying out a solution on a finite difference grid on the accuracy of prediction. This discussion will bring us to the issue of the practical treatment of point and line sources, and thus to the need for a "micro-scale model", that is, a model capable of describing concentration behavior on space and time scales smaller than those employed for the basic model. Finally, we summarize both the attractive features and the shortcomings of the grid model approach to urban airshed modeling.

### a. Numerical Methods

We can classify numerical methods for solution of the diffusion equations (10) in terms of:

- Conventional finite difference methods
- Particle in cell methods
- Variational methods

We will discuss in this section finite difference methods and particle in cell methods. Variational methods involve assuming the form of the concentration distribution, usually in terms of an expansion of known functions, and evaluating coefficients in the expansion. There is currently very active interest in the application of these techniques (Douglas and DuPont, 1970); however, they are not yet sufficiently well developed that they may be applied to the solution of three-dimensional, time-dependent partial differential equations, such as (10). For this reason we will not discuss these methods here.

### (1) Finite Difference Methods

The numerical analysis literature abounds with finite-difference methods for the numerical solution of partial differential equations. While these methods have been successfully applied in the solution of two-dimensional problems in fluid mechanics and diffusion (Crowley, 1968; Fromm, 1969), there is a dearth of reported experience in the solution of three-dimensional, time-dependent, nonlinear problems. Application of these techniques, then, must proceed by extending methods successfully applied in two-dimensional formulations to the more complex problem of solving (10). For general discussions of the various types of finite-difference methods applicable in the solution of partial differential equations, and their advantages and disadvantages, we refer the reader to the books by von Rosenberg (1969), Forsythe and Wasow (1960), and Ames (1969).

The main advantage in using a finite-difference method in the solution of (10), as compared with other approaches, is that there has been extensive experience in applying these techniques to a wide variety of partial differential equations. Even though reported experience with three-dimensional, time-dependent, nonlinear problems is scanty, experience with simpler systems provides a sound basis for the development of feasible approaches. The disadvantages of finite difference methods are well-known:

(a) Inaccuracies in approximating the first-order advection terms in the continuity equations give rise to second-order errors, which have the mathematical characteristics of diffusion processes. These inaccuracies, often termed "numerical" or "artificial" diffusion, can mask the representation of true diffusion. Finite difference methods based on approximations of higher than second order are required to minimize this difficulty; unfortunately, computational times increase with increasing order of the method used.

(b) Computing time and storage requirements associated with accurate, stable methods can be substantial for problems involving several independent variables. When the equations are nonlinear, time-consuming iterations or matrix inversions are often required in the solution.

### (2) Particle in Cell Methods

An alternative to the direct finite-difference solution of (10) is the so-called particle in cell (PIC) technique. The distinguishing feature of the PIC technique is that the continuous concentration field is treated as a collection of mass points, each representing a given amount of pollutant and each located at the center of mass of the volume of material it represents. The mass points, or particles, are moved by advection and diffusion. It is convenient but not necessary, to have each of the particles of a given contaminant represent the same mass of material. The application of the PIC technique in hydrodynamic calculations is discussed by Harlow (1964). The PIC technique has been adapted to air pollution modeling by Sklarew et al. (1971).

The PIC technique has the following advantages:

(a) Artificial diffusion due to truncation errors in the advection terms in (10) is eliminated since these terms are not approximated by finite-difference representations.

(b) There are no stability restrictions on $\Delta t$ (although $\Delta t$ should be small enough so that the value of the particle velocity is representative of the movement of fluid particles).

(c) Particles can be tagged as to their place of origin, thus making it possible to identify the sources of contaminants observed at any location.

and the following weaknesses:

(a) Computer storage requirements can become excessive, as the coordinates of a large number of particles must be kept in memory.

(b) If it is assumed that each particle of a given contaminant represents the same mass of material, then every cell will have a residue that cannot be assigned to a particle. On the average, this residual material will equal one-half of a particle mass. If the assumption that particles be of equal mass is relaxed, the residue error can be eliminated, but only at the cost of storing a large amount of additional information--the masses of all species in each cell.

### b. The Practical Treatment of Point and Line Sources

Application of a grid model requires the numerical solution of the atmospheric diffusion equations. Since the solution is carried out on a digital computer, all continuous variables must be converted to discrete variables. This is accomplished by dividing the region into a three-dimensional net, at each node of which the variables are defined. As we have seen, this process involves spatial averaging over the volume $\Delta x \Delta y \Delta z$ for each grid square. Source emissions are likewise defined only at the grid points, resulting in a similar averaging.

Two of the most important types of sources are point (stacks) and line (roadways). In developing an airshed model, we must immediately deal with the question, "What is the "proper" way of including point and line sources in the source emission function? The key problem arises with sources of reactive pollutants, such as power plants and freeways. It is improper to assume that emissions from these sources are instantaneously and uniformly mixed in the grid square in which they are emitted. This is because the lower levels of concentrations resulting after averaging may lead to reaction rates different than those actually taking place in the more concentrated plume from the source. Nevertheless, this assumption is currently commonly made as a matter of convenience. A procedure for allocating point source emissions in downwind cells has been used by Roberts et al. (1971), although to date no account has been taken of the chemical reactions which are taking place in the plume. Reactions are allowed to occur only after the emissions have been assigned to grid cells.

It is very clear that studies need to be conducted to improve the practical treatment of point and line sources in grid models. These studies can be divided into two areas:

(1) Theoretical - Equations must be developed and solved for a chemically reacting plume, particularly for a plume having high NO and $H_2O$ concentrations that is being emitted into an

atmosphere of hydrocarbons and ozone. Both the fluid mechanics of the plume and the chemistry must be considered. The importance of the effect of concentration fluctuations on the turbulent chemistry should also be assessed.

(2) Experimental - Fundamental information is needed concerning the degree of mixing and dispersion that occurs in plumes from power plants and freeways. Tracer studies can play an important role in elucidating these processes. An experimental program of tracer measurements from freeways in the Los Angeles basin is being conducted by Professor F.H. Shair of the California Institute of Technology. Preliminary results from studies of this type should aid in carefully defining a series of additional tracer studies. These experiments are generally low in cost and and would nicely complement theoretical studies.

## 2. Trajectory Models

As we have noted, the principal feature of trajectory models is that concentration changes in a hypothetical parcel of air are computed as the parcel traverses the airshed. The parcel is visualized as a vertical column of air of fixed area and variable height, with the top of the column being defined by the base of an elevated inversion or, in the absence of an inversion, by an estimated maximum mixing height. The motion of the air column is assumed to correspond to the local instantaneous wind speed and direction, thereby tracing out a particular surface trajectory in the airshed.

The following assumptions are inherent in the model:

(a) There is no horizontal transport of material across the boundaries of the parcel. (There is, in fact, no means of including horizontal diffusive transport between the column and the environment.)

(b) There is no change in the horizontal wind velocity with height.

(c) Vertical advection is neglected, i.e. the vertical component of the wind does not exist.

The basic assumption underlying the approach is that a parcel of air maintains its integrity while traversing the airshed. It is unlikely that this is often the case in the atmosphere over the time scales of interest. Therefore, it is of prime importance to assess the validity of this basic assumption before such a model is used for practical computation. This point will be discussed more fully in Chapter VI.

Referring to Figure 3, consider a volume which is moving through an airshed in such a way that all points on the boundary of the volume move with the mean wind ground-level velocity $\bar{u} = (\bar{u}_1, \bar{u}_2, 0)$ . The vertical movement of the volume caused by vertical velocity components is neglected. Note that the volume pictured in Figure 3 does *not* actually contain the same fluid particles at all times; rather it is merely a hypothetical "cell" moving along with the mean flow. Turbulent mixing across the walls of the cell insures that at each instant there are fluid particles in the cell that were not there previously. In order to assess the validity of assumptions a - c above, we now present an analysis of the trajectory model depicted in Figure 3. In particular, we wish to derive the equations satisfied by the mean concentrations of pollutant species within the volume.

A material balance on species $i$ within a cell of arbitrary volume $V(t)$ which is advected with the mean fluid velocity $\underset{\sim}{u}$ is given by:

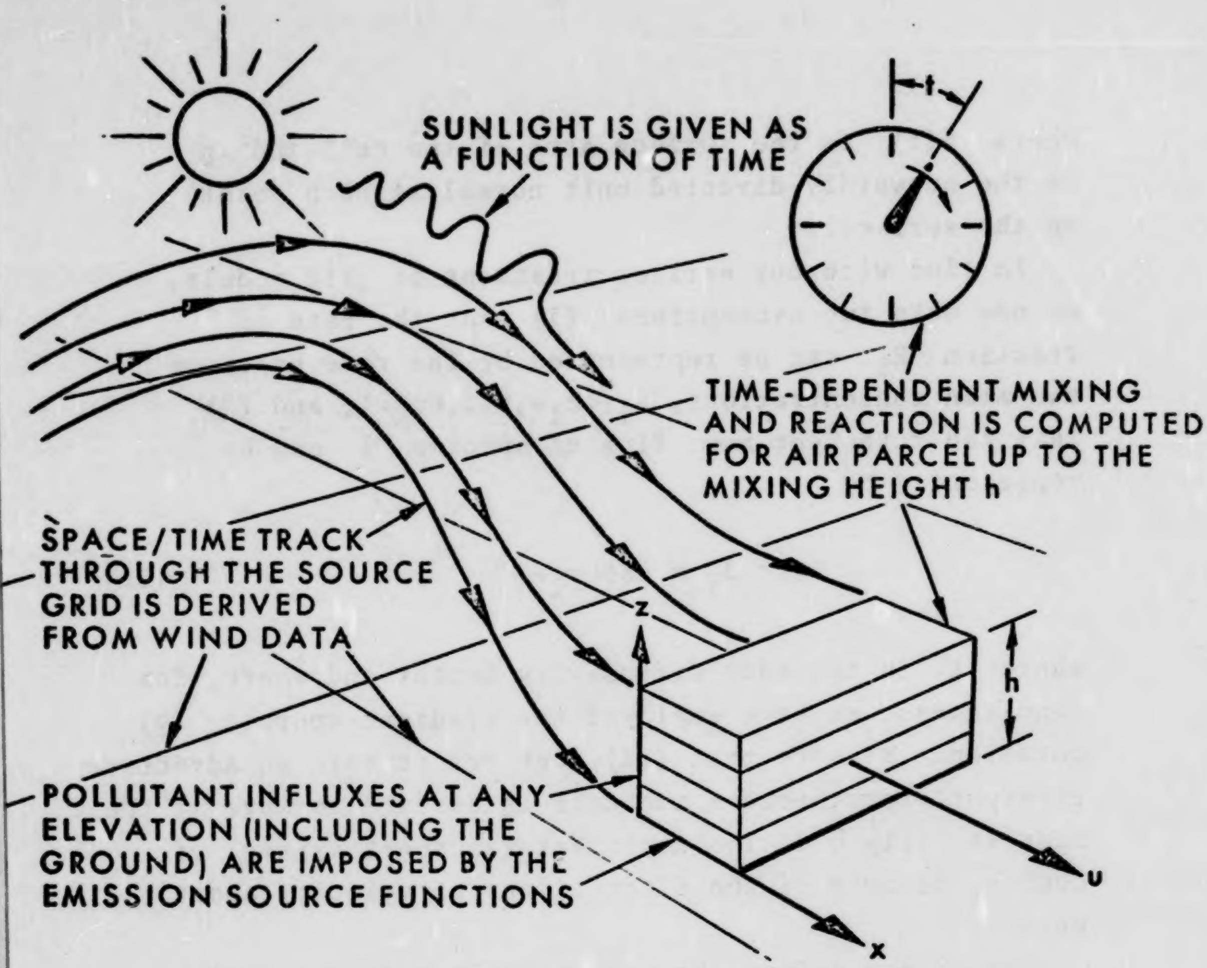
Time rate of change of mass of species $i$ in cell =
Rate of generation of $i$ by chemical reaction +
Rate of introduction of $i$ from sources +
Rate of introduction of $i$ by turbulent mixing
with fluid not contained in the cell at time $t$

We make the following definitions:

$\langle c_i(x,y,z,t)\rangle$ = mean concentration of species $i$ at location $(x,y,z)$ and time $t$ in the fluid
$R_i(c_i,\ldots,c_N)$ = rate of generation of $i$ by reaction
$Q_i(x,y,z,t)$ = rate of emission of $i$ by sources in the fluid
$\underset{\sim}{J}_i(x,y,z,t)$ = turbulent mass flux vector of species $i$

Employing these definitions, the material balance on species $i$ can be written explicitly as

$$\frac{d}{dt}\int_{V(t)} \langle c_i\rangle \, dV = \int_{V(t)} R_i(c_1,\ldots,c_N)\, dV + \int_{V(t)} Q_i \, dV - \int_{S(t)} \underset{\sim}{J}_i \cdot \underset{\sim}{n}\, dS \qquad (22)$$



SUNLIGHT IS GIVEN AS A FUNCTION OF TIME
t
TIME-DEPENDENT MIXING AND REACTION IS COMPUTED FOR AIR PARCEL UP TO THE MIXING HEIGHT h
SPACE/TIME TRACK THROUGH THE SOURCE GRID IS DERIVED FROM WIND DATA
z
h
POLLUTANT INFLUXES AT ANY ELEVATION (INCLUDING THE GROUND) ARE IMPOSED BY THE EMISSION SOURCE FUNCTIONS
u
x

FIGURE 3. A Volume Which Moves Through an Airshed in Such a Way That All Points in the Volume Move With the Mean Wind Velocity.

The drawing, in which the basic elements of a trajectory model for photochemical smog are illustrated, has been taken from Eschenroeder and Martinez (1971).

where $S(t)$ is the surface area of the cell and $\underset{\sim}{n}$ is the outwardly-directed unit normal at each point on the surface.

In line with our earlier treatment of grid models, we now make two assumptions: (1) that the rate of reaction $R_i$ can be represented by the rate based on the mean concentrations, $R_i(\langle c_1 \rangle, \ldots, \langle c_N \rangle)$, and (2) that the turbulent mass flux of species $i$ can be represented by

$$\underset{\sim}{J}_i = -K \nabla \langle c_i \rangle \tag{23}$$

where $K$ is the eddy diffusivity tensor and where, for conciseness, we have employed the gradient operator ($\nabla$) notation. We note that (22) does not contain an advective transport term because the cell is assumed to move at the mean velocity $\bar{\underset{\sim}{u}}$ . The turbulent transport arises, of course, because of the fluctuations of velocity about the mean.

Let us now define the volume-average concentration of the cell at any time $t$ as

$$\bar{c}_i(t) = \frac{1}{V(t)} \int_{V(t)} \langle c_i \rangle \, dV \tag{24}$$

Differentiating $\bar{c}_i$ with respect to time, we get

$$\frac{d\bar{c}_i}{dt} = \frac{1}{V(t)} \frac{d}{dt} \int_{V(t)} \langle c_i \rangle \, dV - \frac{1}{V^2(t)} \frac{dV(t)}{dt} \int_{V(t)} \langle c_i \rangle \, dV$$

$$= \frac{1}{V(t)} \frac{d}{dt} \int_{V(t)} \langle c_i \rangle \, dV - \bar{c}_i(t) \frac{d\ln V(t)}{dt} \qquad (25)$$

Combining (22), (23) and (25), we obtain

$$\frac{d\bar{c}_i}{dt} = \frac{1}{V(t)} \int_{V(t)} R_i(\langle c_1 \rangle, \ldots, \langle c_N \rangle) \, dV + \frac{1}{V(t)} \int_{V(t)} Q_i \, dV$$

$$+ \frac{1}{V(t)} \int_{S(t)} K\nabla \langle c_i \rangle \cdot \underline{n} \, dS - \bar{c}_i \frac{d\ln V(t)}{dt} \qquad (26)$$

Employing the divergence theorem to recast the third term on the R.H.S. of (26) as an integral over the volume, we get

$$\frac{d\bar{c}_i}{dt} = \frac{1}{V(t)} \int_{V(t)} \{ R_i(\langle c_1 \rangle, \ldots, \langle c_N \rangle) + Q_i + \nabla \cdot K\nabla \langle c_i \rangle \} \, dV$$

$$- \bar{c}_i \frac{d\ln V(t)}{dt} \qquad (27)$$

If it is now assumed that the volume-averaged rate of reaction can be equated to the rate of reaction of the volume-averaged concentrations, i.e.

$$\frac{1}{V(t)}\int_{V(t)} R_i(<c_1>,\ldots,<c_N>)\, dV = R_i(\bar{c}_1,\ldots,\bar{c}_N) \qquad (28)$$

which in general is unjustified because $R_i$ is nonlinear, (28) becomes

$$\frac{d\bar{c}_i}{dt} = R_i(\bar{c}_1,\ldots,\bar{c}_N) + \frac{1}{V(t)}\int_{V(t)} Q_i dV + \frac{1}{V(t)}\int_{V(t)} \nabla\cdot K\nabla<c_i>\, dV$$

$$- \bar{c}_i \frac{d\ln V(t)}{dt} \qquad (29)$$

We see that if the contribution of turbulent diffusive mixing to the time rate of change of the volume average concentration $\bar{c}_i$ in the cell is to be included, the gradient of mean concentration, $\nabla<c_i>$ , within the cell must be known in order to evaluate the third term on the R.H.S. of (29).

Two groups, Eschenroeder and Martinez (1971) and Wayne et al. (1971), have reported results based on a trajectory model. In each case the model involves a column of fixed base area (say 1 $m^2$) and variable height, depending on the depth of the well mixed layer. Eschenroeder and Martinez have allowed the volume-average concentration $\bar{c}_i$ to be an average across a plane at constant $z$ , i.e. $\bar{c}_i(z,t)$ , in order to include the vertical component of the turbulent mass flux. The form of (38) employed their model is

$$\frac{\partial \bar{c}_i(z,t)}{\partial t} = R_i(\bar{c}_1,\ldots,\bar{c}_N) + \frac{1}{V(t)}\int_{V(t)} Q_i\,dV + \frac{\partial}{\partial z}\left(K_V \frac{\partial \bar{c}_i}{\partial z}\right) \tag{30}$$

where horizontal turbulent diffusion has been neglected. The initial condition for (30) is that the concentration within the column at the beginning of the traversal be given, i.e.,

$$\bar{c}_i(z,0) = c_{i_o}$$

The boundary conditions on $z$ at the ground, $z = 0$, and the inversion base (on top of the column), $z = H(t)$, are given by

$$-K_V(0)\frac{\partial \bar{c}_i}{\partial z} = Q_i(x,y,0,t) \qquad z = 0$$

$$-K_V(H)\frac{\partial \bar{c}_i}{\partial z} = 0 \qquad z = H(t)$$

where $H(t)$ is the height of the column as a function of time. The movement of the column is reflected mathematically only in $Q_i$ and $H$.

Wayne et al., in their formulation, have also neglected horizontal turbulent diffusion and have, in addition, assumed vertical homogeneity. Thus, their model is based on

$$\frac{d\bar{c}_i}{dt} = R_i(\bar{c}_1,\ldots,\bar{c}_N) + \frac{1}{V(t)}\int_{V(t)} Q_i\,dV - \bar{c}_i\,\frac{d\ln V(t)}{dt} \tag{31}$$

where the column is simply a well-mixed cell of fixed base area and variable height. The advantage of (31) over (30) is purely computational, since (31) consists of a set of ordinary differential equations rather than a set of partial differential equations. Since (30) does not involve an assumption of vertical homogeneity, it is clearly more general than (31).

The essential virtue of the trajectory model is its simplicity, since it is computationally advantageous to avoid the integration of the diffusion equations in three spatial dimensions and time. However, it is important to stress that the trajectory model is *not* a full airshed model, nor is it intended as such. Rather, it is a technique for computing concentration histories along a given air trajectory. It is not feasible to use this approach, even if its validity could be established to predict concentrations as a function of time and location throughout an airshed, since a very large number of trajectory calculations would be required.

Let us conclude this discussion by summarizing the main assumptions inherent in the trajectory models now in use, e.g. that of Eschenroeder and Martinez (1971):

1. The contribution of horizontal turbulent diffusion to the time rate of change of concentration in the parcel is small relative to that of sources and chemical reactions. In effect, this assumption is tantamount to treating the parcel as an identifiable and integral parcel of air over the course of a trajectory traversal.

2. The parcel moves with the mean ground-level *horizontal* wind velocities. Thus, vertical components in the velocity field are neglected.
3. Changes in wind velocity and direction with height are ignored. The parcel is assumed to have a constant volume and shape over the course of a trajectory.
4. The volume-averaged rate of chemical reaction is based on the rate depending on the volume-averaged concentrations.

While trajectory models have been employed in the urban-scale modeling, their validity has yet to be firmly demonstrated. The most serious deficiencies are the neglect of horizontal diffusion in the model and the inability to accommodate a truly three-dimensional wind field. A theoretical evaluation of the effect of these deficiencies on the predictions of the model is needed before extensive studies are carried out using these models.

## 3. Summary of Current Urban Airshed Models for Photo-Chemical Air Pollution

We present in Table 6 a summary of urban airshed models that may be used for predicting ground level concentrations of reactive contaminants. Detailed descriptions of the models may be found in the references cited.

TABLE 5. Summary of Urban Airshed Models for Photochemical Air Pollution

| Reference | Description of Model | Reported Results |
|---|---|---|
| Eschenroeder and Martinez (1971) | Trajectory model. Model based on moving column of air in which vertical diffusion and chemical reactions take place. Column of air follows a surface trajectory interpolated from monitoring station wind readings. EM kinetic mechanism used. | Applied to Los Angeles for CO, NO, $NO_2$, HC, $O_3$. Various wind trajectories on six validation days. |
| Wayne et al. (1971) | Trajectory model. Model based on moving column of air which is well mixed and in which chemical reactions take place. Column of air follows a surface trajectory interpolated from monitoring station wind readings. Wayne kinetic mechanism used. | Applied to Los Angeles for CO, NO, $NO_2$, HC, $O_3$. Various wind trajectories on six validation days. |
| Roth et al. (1971) | Grid model. Model based on numerical solution of the three-dimensional, time-dependent atmospheric diffusion equations. Numerical solution based on the method of fractional steps. HS kinetic mechanism used. Three-dimensional wind field computed from surface maps. | Applied to Los Angeles for CO, NO, $NO_2$, HC, $O_3$. Complete spatial and temporal distributions over basin for six validation days. |
| Sklarew et al. (1971) | Grid model. Model based on numerical solution of the three-dimensional, time-dependent atmospheric diffusion equations. Numerical solution based on particle-in-cell method. EM kinetic mechanism used. Three dimensional wind field computed from surface maps. | Applied to Los Angeles for CO, NO, $NO_2$, HC, $O_3$. Complete spatial and temporal distribution over basin for one validation day. |
| McCracken et al. (1971) | Cell model. Model based on solution of dynamic mass balance equations for an interconnected array of well-mixed cells. Gear's method used in numerical integration of coupled, ordinary differential equations. Two dimensional wind field and assumed vertical velocity profile used. | Applied to San Francisco Bay Area for CO. Complete spatial and temporal distribution over Bay Area for two consecutive days. |

## D. Levels of Uncertainty in Input Variables

A necessary part of the development of any model is an assessment of the levels of uncertainty in each of the input variables and the effect of these uncertainties on the predictions of the model. In this section it is our objective to enumerate those inputs to an urban airshed model for which estimates of accuracy are particularly important. In addition, we shall also consider the levels of uncertainty in the concentration data reported at monitoring stations against which the model is to be ultimately compared.

Certain input components can be estimated with considerably greater accuracy than others. For example, an automotive emissions inventory is, in general, based on a much richer data base than are urban wind field maps. Because of the large amount of data available for constructing an inventory of automotive emissions and because of the importance of motor vehicle emissions relative to other sources in areas plagued by photochemical smog, considerably greater attention has been devoted to this source in the compilation of inventories for use in urban airshed modeling. The relative paucity of data involving other source emissions in particular and involving other model inputs in general is a serious deficiency requiring future attention.

### 1. Levels of Uncertainty in Source Emissions

The first step in the validation of an urban air pollution model is the compilation of a complete contaminant emissions inventory for the area of interest. We can divide source emissions according to:

a. Automotive Emissions
  (1) Spatial distribution of traffic
  (2) Temporal distribution of traffic
  (3) Exhaust emissions
    (1) Freeway traffic
    (2) Non-freeway traffic
  (4) Crankcase emissions
  (5) Evaporative emissions
b. Fixed source emissions
  (1) Power plants
  (2) Refineries
  (3) Other fixed sources
c. Aircraft emissions*

### a. Automotive Emissions

Let us assume that the airshed has been divided into a grid and that we desire to calculate the mass of each contaminant emitted from motor vehicles into each surface cell as a function of time. For each cell this quantity can be computed, in principle, as the product of $M_\ell$ , the total vehicle miles traveled in the grid square in hour $\ell$ , and $Q_k$ , the grams of species $k$ emitted per mile by an "average" vehicle. Actually, it is useful to differentiate between freeway and non-freeway vehicle mileage because the driving characteristics, and hence, vehicle emission rates, vary for each.

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*We will not consider aircraft emissions here. While these emissions may have a significant effect on the atmosphere in the vicinity of an airport, contributions from aircraft to the total emissions of an airshed are generally no more than a few percent.

Both the spatial and temporal distribution of traffic may be determined from traffic count data taken as numbers of vehicles per hour passing a specified location along the roadway. Using traffic count data at a number of points along a given artery, the number of vehicle miles per day traveled on the artery can be determined. Such traffic count data are readily available from the traffic department of any large city.

The first issue to be faced in compiling an "inventory" of traffic involves the level of detail to incorporate. For example, should one include traffic counts only for freeways and major and minor arteries, ignoring residential and side streets, or for all streets for which data are available. Since this effort is undertaken only once, it is recommended that the inventory be made as complete as possible. Traffic flow can be estimated on small streets, for which data are unavailable, from local traffic data in the area, the type of neighborhood, and reference to counts on similar types of streets.

For a given grid square the vehicle miles per hour $M_\ell$ (for the $\ell$th hour) traveled on all roads in the cell can be computed from:

$$M_\ell^f = d_\ell^f \sum_{u=1}^{s^f} n_u^f t_u^f \qquad \text{freeways}$$

$$M_\ell^s = d_\ell^s \sum_{u=1}^{s^s} n_u^s t_u^s \qquad \text{surface streets}$$

where

$n_u$ = vehicles per day (given as traffic counts at a point, assignable to a segment of road), f = freeway, s = surface streets

$t_u$ = miles of road segment to which the count $n_u$ is assigned

$d_\ell$ = fraction of the daily (24-hour) traffic count assignable to hourly period $\ell$ ; $\sum_\ell d_\ell = 1$ .

s = number of road segments contained in the grid square, $s^f$ = freeway, $s^s$ = surface streets

$M_\ell = M_\ell^f + M_\ell^s$

A determination of $M_\ell$ for week day traffic, compiled for a grid of 2 mi x 2 mi squares for Los Angeles, has been reported by Roberts et al. (1971). They estimated $M_\ell$ for each grid square to be accurate to 5-10%. Thus, a figure of 400,000 vehicle miles/day, for example, should be interpreted as 400,000 ± 40,000 if the accuracy were ± 10%.

It is commonly accepted that the hourly variation in weekday traffic flow may be represented over a 24-hour period by a bimodal distribution having peaks at the morning and afternoon rush hours and a high plateau between these peaks. However, the parameters needed to describe this distribution--the height of each peak, the height of the plateau, the time interval encompassing each peak--vary from street to street. Shopping areas have a high frequency of traffic between peak hours. Streets in lower middle class neighborhoods experience earlier morning and afternoon peaks than do streets in upper middle class neighborhoods. Downtown streets carry light traffic following the afternoon peak, whereas suburban and residential arterials have higher traffic loads at this time.

Ideally we would like to compute a separate $d_\ell^f$ and $d_\ell^s$ for each grid square appropriate to the traffic patterns in that square. Since the grid square, the smallest spatial unit in the airshed model, usually contains streets of many classifications, an average of the temporal traffic distributions over all the streets in the square would, in all likelihood, provide a satisfactory estimate for $d_\ell^f$ and $d_\ell^s$ for that square. A less time-consuming alternative, however, is to determine airshed-wide "grand" distributions, $d_\ell^f$ and $d_\ell^s$ , by averaging the hourly distributions of traffic counts compiled for a sufficiently large number of randomly selected city streets (the sample being stratified according to the magnitude of the daily traffic flow), the counts on individual streets being weighted in proportion to the magnitude of traffic flow on the street. While convenient, this alternative is obviously less desirable than determining square-by-square distributions, where the effect of differences in traffic flows between central city and suburbs can be included.

Roberts et al. (1971) have developed "grand" temporal distributions, $d_\ell^f$ and $d_\ell^s$ , for Los Angeles. In order to judge the accuracy of the grand distributions, the statistically derived distribution was multiplied by the total daily vehicle mileage for one chosen grid square. These *calculated* hourly vehicle mileages were then compared with hourly vehicle mileages for the same grid square, determined using *actual* houly traffic counts. The calculated discrepancies in surface street vehicle mileage for each time period for the grid square in the Wilshire/LaBrea area were:

| Time Period | Discrepancy | Approx. Percentage of Daily Traffic Flow |
|---|---|---|
| 6-7 a.m. | -10.5% | 3% |
| 7-9 a.m. | 0.3 | 13 |
| 9-11 a.m. | -7.0 | 10 |
| 11 a.m.-4 p.m. | 4.0 | 30 |
| 4-6 p.m. | -6.0 | 16 |
| 6-8 p.m. | -3.1 | 11 |

Based on the Los Angeles results, the estimated uncertainties in the grand distributions are:

$d_\ell^f$: ± 2-4%  $d_\ell^s$: ± 5-7%

During the period when vehicular emissions were uncontrolled, automobile exhaust emissions accounted for approximately 65% of automotive hydrocarbon emissions and 100% of CO and $NO_x$ emissions. As a result of vehicle modifications and changing legislation through the 1960's and 1970's, the magnitudes and relative amounts of these three pollutants vary with model year.

We turn now to consideration of exhaust emissions. The basic premise underlying exhaust emission calculations is to determine for the airshed an "average" vehicle and an "average" trip. The "average vehicle" is found by averaging over the total vehicle population, taking into account model year, manufacturer, weight and transmission type (automatic or manual). The average trip is chosen as being representative of the driving habits of the airshed population. The trip, usually termed a *driving cycle*, is composed of a series of driving modes (idle, accelerate, cruise, and decelerate) in which a pre-determined length of time is spent in each mode. Such a cycle is formulated by "tagging" a large number of vehicles on a particular day and analyzing their trips, including the time spent in each mode. A recent study of this type has been reported by Smith and Manos (1972). The emissions from a large population of automobiles are measured as the vehicles are run through the cycle on a chassis dynamometer and the resulting average yields a set of figures for each automobile type--the grams of pollutant $k$ emitted per mile. Averaging over the total vehicle population yields $Q_k$ , the grams of species $k$/mile emitted by the "average" vehicle when driven over the "average" cycle.

Several test procedures for measuring exhaust emissions have been proposed in recent years. These procedures have as their common aim the simulation of emissions in a stationary test of a vehicle being operated in traffic. There is currently considerable debate concerning the degree to which the various test procedures are representative of actual vehicular emissions, or, indeed, if it is possible to simulate the emissions of a vehicle by any test procedure. A choice must also be made between the use of a hot start and a cold start procedure.

A method which has enjoyed widespread use in recent years, including adoption as the Federal testing procedure up to 1971, is the California Driving Cycle (CDC). This is a seven-mode test procedure and is based on a Los Angeles commuter run (see State of California ARB (1968)). Recently, however, the representativeness of the CDC has been questioned, and a new method, the 1972 Federal test procedure, has been proposed. This procedure employs a cold start and a driving cycle (the LA-4 cycle) derived from a Los Angeles driving route during heavy traffic periods. Actual mass emissions are monitored over the entire driving cycle, in contrast to the CDC, in which concentrations are measured. The differences between the three procedures--hot start and cold start CDC and 1972 Federal procedure--are illustrated by the following figures (Sigworth (1971)):

|  | Approximate increase in emissions rates when measured by cold start CDC, as compared with hot start CDC (all vehicles). | Approximate increase in emissions rates when measured by 1972 Federal procedure, as compared with *cold* start CDC. |  |
|---|---|---|---|
|  |  | Pre-1966 vehicles | 1966-1969 vehicles |
| HC | + 30% | + 40% | + 90% |
| CO | + 0-10% | + 60% | + 100% |
| $NO_x$ | - 5% | + 60% | + 30% |

It is apparent from these figures that measured emissions rates are strongly dependent on the testing procedure employed.

Values of $Q_k$ for the 1969 Los Angeles vehicle population have been computed by Roberts et al. (1971, 1973) using the CDC and the FDC. The results were:

| Species | CDC | FDC |  |
|---|---|---|---|
|  | Hot Start | Hot Start | Cold Start |
| CO | 63.9 gm/mi. | 68.6 gm/mi. | 91.0 gm/mi. |
| HC (exhaust + blowby) | 9.0 | 10.8 | 11.7 |
| $NO_x$ (as NO) | 2.9 | 2.7 | 2.7 |

It is our belief that by far the greatest uncertainty in the calculation of motor vehicle emissions is attributable to our inability to assess the representativeness of a driving cycle in a particular locale. Recently, the FDC has replaced the CDC as the standard emissions test procedure. Nevertheless, the representativeness of the FDC or any other cycle has yet to be demonstrated. We recommend that studies such as those reported by Smith and Manos (1972) be undertaken for cities for which urban airshed models are to be developed.

### b. Fixed Source Emissions - Power Plants and Refineries

The principal problem associated with fixed source emissions is a lack of data. Few measurements of effluent concentrations are made, and there are virtually no data available that reflect the effect of process variations on emissions rates. In addition, temporal variations, particularly in the operation of power plants, are often considerable, yet unpredictable, since they frequently depend on such unreliable and capricious factors as the weather.

Generally, highly simplified assumptions are made in estimating emissions rates from large "point sources" in an urban area. For example, emissions rates from refineries are usually assumed to be directly proportional to the crude throughput rate. This rate is not only assumed uniform over a day (uniform temporal distribution), but usually represents an average taken over a period of one month to a year. Data related to emissions from power plants is generally easier to obtain, and often is fairly complete (see, for example, that computed for Los Angeles by Roberts et al. (1971,1973)). However, measurements made for one day are generally assumed to apply for all days, corrected for daily temporal distribution and season (summer vs. winter); the validity of this assumption remains in question.

The following types of data are needed to estimate emissions rates from power plants:

1) electric capacity of plant (megawatts)
2) mass flow of flue gas (pounds/hr)
3) volume flow of flue gas (cubic ft./min.)
4) effluent temperature
5) volume concentration of $NO_x$ and $SO_2$ (ppm)
6) likely temporal distribution of operation

Similar data are needed to estimate emissions from refinery process units, although temporal variations (on a daily basis) are likely to be unimportant. In addition, emissions and evaporative losses of both reactive and unreactive organic gases must be estimated, the latter being particularly difficult to determine.

In general, then, emissions data from power plants, while of variable quality (from quite good to rather poor), are generally available. Refinery emissions data are usually unavailable, and thus estimates of emissions from this class of sources are highly uncertain (perhaps up to ± 100% or more). Inaccuracies in emissions rates from large, concentrated or point sources can have a noticeable impact in model prediction, particularly in the case of $NO_x$ . In Los Angeles, for example, over 25% of $NO_x$ emissions emanate from power plants and refineries. See Roberts et al. (1971, 1973) for an example of a fixed source emissions model and inventory.

## 2. Level of Accuracy of Meteorological Data

Meteorological data needed in model validation can be classified as follows:

1) Vertical variation of temperature as a function of time and location
2) Three-dimensional wind field as a function of time.

The vertical variation of temperature must be known to determine the height of an inversion layer, as well as to establish the importance of buoyancy-generated turbulence relative to mechanically generated turbulence. The temperature profile is of interest in the latter instance because it is related, to a degree, to the magnitude of the vertical eddy diffusivity $K_V$. In most urban areas there is virtually a total lack of vertical temperature profile data. Thus, the upper limit for mixing must be estimated, at best on the basis of one or two soundings taken during the day at one location (often at the airport, which is generally not centrally located relative to the urban area). For an inland city, these few soundings may be sufficient to permit specification of the mixing depth, since the temperature profile aloft at any given time should not vary substantially with location. However, for a coastal area, such as Los Angeles, there are significant spatial, as well as temporal, variations in the mixing depth. For example, at 1 PM on a given day, the mixing depth at Santa Monica can be one-fourth that at El Monte, 25 miles east. Thus, in such areas, soundings at one location are not sufficient to specify the inversion behavior.

In the Los Angeles area soundings are currently made at two locations in the Basin, Los Angeles International Airport and El Monte, twice a day--at approximately 6 AM and 11 AM. Using these data, fairly accurate estimates of mixing depth may be made during the morning hours for the greater part of the Los Angeles Basin. But the height of the inversion base is not known in the afternoon, nor is it known over certain highly populated areas, such as the San Fernando Valley and Orange County. Hence, it can be estimated only with great uncertainty at these times and over these areas. As a second example, rawinsonde measurements have traditionally been made no closer than 100 miles to St. Louis, at Columbia, Missouri. The degree to which these measurements represent the actual profiles over St. Louis clearly must be established. (With the advent of the RAPS program, vertical temperature profiles will be measured over the city on a routine basis.)

We now turn our attention to wind data. The wind field is determined by interpolation of wind station readings. The density of stations needed for adequate interpolation depends on the terrain of the airshed; a denser net of stations is required when the terrain is hilly or mountainous. Most urban areas do not have a wind monitoring system adequate for preparing a ground-level wind field having spatial resolution comparable to that of a model.

The greatest errors in wind speed measurement occur at low speeds; in this range errors of 100% are not uncommon. Wind direction, usually measured accurately at moderate speeds, can also be a problem at low speeds. The largest uncertainty arises in estimating winds aloft, both in speed and direction, as such data are generally unavailable. In fact, the specification of winds aloft probably represents at this time the largest source of error in an urban airshed model.

## 3. Level of Accuracy of Reported Airshed Data

As part of its current Los Angeles modeling program, SAI has reviewed the concentration measurement techniques employed by the Los Angeles APCD in terms of accuracy, specificity, and reliability. In general, accuracies in determination of the concentration of any pollutant are no better than ± 10%. Degree of specificity and reliability varies greatly, depending upon the measurement. The following tentative conclusions have been drawn with regard to the use and interpretation of the APCD data:

| | |
|---|---|
| CO | no correction needed |
| NO | the oxidation of NO to $NO_2$ and subsequent colorimetric measurement of the product $NO_2$ is 70-85% efficient. Thus, reported NO concentrations must be increased by about 20% for use in validation. |
| $NO_2$ | PAN interferes with measurement of $NO_2$. Accuracy of measurements is ± 10-20%. No correction is recommended due to lack of information -- knowledge of PAN concentration and other sources of error.* |

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*Although not presently in routine use, chemiluminescence techniques, which are more specific than methods currently employed by control agencies, are now available.

| | |
|---|---|
| Oxidant | Methods in use are not specific for ozone; contributions of $NO_2$, PAN, and other specific oxidants must be subtracted from the total reading. Presence of $NO_2$ increases oxidant readings by 10-20% of the $NO_2$ concentration; $SO_2$ decreases readings by an amount approximately equal to $SO_2$ concentration.* |
| Total Hydrocarbons | Flame ionization is specific for carbon, recording oxygenated hydrocarbons as well as hydrocarbons. Readings are difficult to interpret because: i) calibration is carried out using a specific hydrocarbon (APCD uses methane), whereas the hydrocarbons measured are a complex mixture. While it is assumed that response is proportional to number of carbon atoms, significant deviations from this assumption have been observed. ii) methane is by far the dominant constituent, making determination of non-methane constituents by difference an uncertain matter. iii) variation in reactivity with type of HC affects measurement. At this time, total hydrocarbon measurements are probably too uncertain to be useful in model validation. |

In addition to these problems of measurement, there exist two fundamental problems related to sampling:

1) Unless a sample is taken instantaneously, it will generally contain a mixture of contaminants that is not necessarily representative of the pollutant concentrations at the monitoring site at the reported time of sampling.

2) If the time lag associated with collection and and analysis is long, then the possibility that further chemical reaction has taken place in the sample gases must be considered. Thus, time lags must be taken into account in analysis of data.

We will return to questions of instrumentation and measurement in Chapter V when we discuss smog chamber experiments.

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* See footnote on preceding page.

## 4. The Problem of Disparate Scales

Clearly, uncertainties in emissions and meteorological data can only serve to degrade the quality of predictions provided by an urban airshed model. And uncertainties in air quality data can only enhance discrepancies between prediction and measurement in model validation. However, an additional factor contributes to the difficulties that inhere to validation, the inappropriateness of comparing "point" measurements with spatially averaged predictions.

Consider, as an example, the validation of an urban airshed model, where carbon monoxide is the pollutant of concern. Suppose that the model is based on the assumption that emissions are uniformly distributed in space and time (over an hourly interval) over cells of appropriate horizontal dimension (say 2 miles x 2 miles), and that meteorological conditions are also invariant over this scale. The direct result of these assumptions is that *the predicted pollutant concentrations* are uniform within each grid square (or cell). *The observed values* of CO, however, typically are representative only of the CO concentrations in the immediate vicinity of the sampling site (perhaps, a range of 20 to 200 feet). Of the ten monitoring stations operated by the Los Angeles County APCD, seven are located within 100 feet of a roadway having a daily traffic count in excess of 15,000 vehicles. Ott (1971) has shown that CO concentrations measured at a monitoring station situated along a busy city street are approximately twice the background level

(400 feet or more away from the street) and slightly more than half that measured at the sidewalk located between the street and the station. While we may expect that a properly formulated urban scale model will predict background levels with reasonable accuracy over the scale selected, there is no justification for comparing these predictions with local point observations. We refer to the inappropriateness of comparing predicted and measured concentrations as "the problem of disparate scales".

Some basis for comparison is required, however, if the validity of the model is to be established. Either background observations may be made, or a model may be developed that is capable of predicting concentrations at a nearby point that are due to local emissions. As it is currently virtually impossible to make area-wide (2 mile x 2 mile or similar) measurements,* it is necessary to develop models of subgrid scale phenomena to resolve the problem. Such models may be incorporated in an urban scale model, or exercised independently.

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* Remote measurement from satellites may provide a means for making area-wide measurements. However, the equipment, techniques, and systems required are not yet well enough developed to be implemented.

## 5. Other Sources of Inaccuracy

Three sources of inaccuracy, other than those discussed thus far, plague modeling -- establishment of initial conditions, specification of boundary conditions, and estimation of hydrocarbon reactivity. We discuss each briefly.

Initial conditions at the ground may be established by interpolating measured concentrations made at the time of interest. Inaccuracies may be great in certain areas, however, depending upon the location and spacing of the monitoring stations. In general, no measurements are available for establishing initial conditions aloft; these can only be guessed. A common practice is to assume that initial conditions at any point $(x,y,z)$ are equal to those directly below, i.e., at the surface at location $(x,y,0)$. While this assumption may be satisfactory (though not necessarily accurate) during the day when the atmosphere is often reasonably well mixed, it is probably not valid during the early morning hours (a time when most model solutions are initialized) due to the lack of vertical mixing.

The only information generally available for specifying boundary conditions, both at the ground and aloft, are those concentrations measured at sites near the boundaries. By chance the location of sites might, on occasion, be suitable; however, such occurrences are fortuitous. Thus, unless boundaries are selected so as to pass through regions where conditions may be estimated with some ease (such as over a large body of water), the specifications of concentrations at the boundary is a highly uncertain undertaking. (See, for example, Chapter II of Reynolds et al. (1973).)

Hydrocarbon reactivity may be established if the composition of hydrocarbons in the atmosphere, for any specific mode of grouping, is measured. Gas chromatographic analysis provides the means for obtaining the required data. However, such analyses are never performed routinely because they are involved and complex and require a large manpower commitment. While Eschenroeder and Martinez (1970) have found that the average hydrocarbon reactivity (excluding methane) of the atmosphere is approximately constant over a day in the Los Angeles area, it remains important to determine the atmospheric hydrocarbon reactivity by groups (such as for the groupings suggested in Chapter II) if mechanisms of the sophistication of that shown in Table 4 are to be included in airshed models.

### E. Relationship of Kinetic Mechanisms to the Urban Airshed Model

In order to use (10) as the basis of an urban airshed model, one must be aware of the restrictions that exist on the time scale of the chemical reaction processes described by $R_i$ (see Table 5). In particular, the time scale for the reactions should be large compared to the temporal resolution of (10). We have already presented in Chapter II a detailed discussion of photochemical kinetic models. The criteria which guided the development of the generalized mechanisms discussed in Chapter II dealt primarily with measures of accuracy in prediction of observed chemical behavior and of parsimony with respect to the number of individual species included in the mechanism. Given the restrictions on $R_i$ and the kinetic mechanisms developed or referred to in Chapter II, a basic question must be faced. Are the lumped kinetic mechanisms in common use compatible with the time-scale requirements on $R_i$ that must be satisfied if (10) is used as an urban airshed model?

The purpose of this section is to explore the issue of the time scales associated with various kinetic mechanisms for photochemical smog in order to assess the appropriateness of their inclusion in an overall airshed model based on (10). In other words, we wish to examine whether the degree of detail incorporated in the kinetic portion of the overall model is consistent with the degree of detail in the remainder of the model. The kinetic mechanism enters the overall model (10) through the specification of the functional form of $R_i(c_1,\ldots,c_N)$. Thus, we shall be specifically interested in how the restrictions on $R_i$ are related to restrictions on the structure of the underlying kinetic mechanism from which the $R_i$ are derived.

In Table 5 we indicated that in order to use (10) as an urban airshed model the time scale of the chemical reaction processes should be long compared to the temporal resolution of the model. Let us now quantify this condition. Given values of the mean concentrations, we can represent $R_i(<c_1>,\ldots,<c_N>)$ as $R_i(\underset{\sim}{x},t)$ , a "generation" or "source" term analogous to $S_i(\underset{\sim}{x},t)$ , in (10). Let the time increment for numerical solution of (10) be $\Delta t$ . It can be shown (Lamb and Seinfeld, 1973) that $\Delta t$ must satisfy the conditions:

$$T_L << \Delta t << T_C$$

where $T_L$ is the Lagrangian time scale of the turbulence and $T_C$ is a characteristic time for changes in the concentration field. Typical values of these three times might be

$$T_L \sim 1 \text{ min.}$$

$$\Delta t \sim 10 \text{ min.}$$

$$T_C \sim 1 \text{ hr.}$$

The condition stated at the beginning of this paragraph can be quantitatively written as

$$\frac{1}{R_i(\underset{\sim}{x},t)} \frac{\partial R_i}{\partial t} << \frac{1}{\Delta t} \qquad i = 1,2,\ldots,N \qquad (32)$$

Since $R_i$ is not an explicit function of time, it is difficult to verify this condition directly or to determine how such a restriction might influence the form relation of $R_i$ . For this reason, we must resort to an alternative means of judging whether or not a particular $R_i$ satisfies (32). To do this, let us consider the batch chemical reaction system

$$\frac{dc_i}{dt} = R_i(c_1,\ldots,c_N) \qquad i = 1,2,\ldots,N \qquad (33)$$

and attempt to obtain a measure of the time scale associated with such a system. By a time scale we specifically mean a characteristic time interval over which concentration changes might occur in a chemical system governed by (33). The concept of a characteristic time scale can be seen by considering the decay of a single species by a first order reaction. In this case

$$\frac{dc}{dt} = -kc$$

and

$$c(t) = c(0)e^{-kt}$$

Thus, $c(t)$ decays exponentially, a measure of the time scale of which is $k^{-1}$ (e.g. $c(t)$ decays to $1/e$ of its initial value in a time equal to $k^{-1}$ ). For coupled sets of first order reactions, the solutions for concentrations take the general form

$$c_i(t) = \sum_{j=1}^{N} \alpha_{ij} e^{-\lambda_j t} \qquad i = 1,2,\ldots,N$$

The parameters $\lambda_1,\ldots,\lambda_N$ are called the *eigenvalues* of the system of linear reaction rate equations. When written in the condensed form,

$$\frac{d\underset{\sim}{c}}{dt} = \underset{\sim}{A}\underset{\sim}{c}$$

the eigenvalues $\lambda_1,\ldots,\lambda_N$ are merely the eigenvalues of $\underset{\sim}{A}$ . The time scales for the reactions are given by $\lambda_1^{-1},\ldots,\lambda_N^{-1}$ .

By analogy to the example of sets of linear reactions, the time scales for nonlinear reactions can be given by the eigenvalues of the nonlinear differential equations. The eigenvalues, $\lambda_1,\ldots,\lambda_N$ of a set of nonlinear ordinary differential equations are those of the $N \times N$ Jacobian matrix $\underset{\sim}{J}$ , the $i$ , $j$th element of which is $\partial R_i/\partial c_j$ , and are the $N$ solutions of the equation, $\det (\underset{\sim}{J} - \lambda \underset{\sim}{I}) = 0$ .

Table 7 presents the eigenvalues of the reaction rate equations corresponding to the HS mechanism in Table 1 (differential equations for HC, NO, $NO_2$ and $O_3$). In spite of the

TABLE 7. Eigenvalues of the HS Mechanism (Lamb and Seinfeld, 1973)

| t,min | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\lambda_4$ |
|---|---|---|---|---|
| 1.3 | -33.1 | $4.63 \times 10^{-2}$ | $1.24 \times 10^{-4}$ | $1.28 \times 10^{-7}$ |
| 60.3 | -21.2 | $3.51 \times 10^{-2}$ | $4.83 \times 10^{-4} - 6.59 \times 10^{-4} i$ | $4.83 \times 10^{-4} + 6.59 \times 10^{-4} i$ |
| 119 | -21.5 | $-8.98 \times 10^{-3}$ | $-2.04 \times 10^{-2} - 1.71 \times 10^{-2} i$ | $-2.04 \times 10^{-2} + 1.71 \times 10^{-2} i$ |

NOTE: Initial conditions used were $C_{NO_2}(0) = 0.04$, $C_{NO}($[illegible] $= 1.5$, $CO_3(0) = 0$, $C_{HC}(0) = 3.0$.

fact that the pseudo-steady state approximation has been employed for the free radical species, there is still a broad range in the magnitudes of the eigenvalues. After one minute the component of the linearized solution corresponding to $\lambda_1$ will have a magnitude the order of $e^{-30}$ and will be negligible. Thus, the important rate determining eigenvalue is $\lambda_2$, which is of the order of $10^{-2}$ min.$^{-1}$.

The condition that $\lambda_2^{-1} >> \Delta t$ implies that $\Delta t \leq 10$ min. Fortunately, this estimate is consistent with the estimate for the probable magnitude of $\Delta t$ given earlier. Therefore, we can conclude that the HS (and EM) mechanism is compatible with the time scale requirements of (10). Proposed kinetic mechanisms should be evaluated using requirements of the type $\lambda_i^{-1} >> \Delta t$, where $\lambda_i$ is the rate-determining eigenvalue of the system. Such evaluations may indeed indicate that a kinetic mechanism that adequately matches smog chamber data may be inappropriate for use in conjunction with an airshed model. (For example, the specific mechanisms noted in Chapter II would undoubtedly contain more detail than is compatible with the other portions of the airshed model.)

## F. Suggested Studies

As a result of this discussion of urban airshed models, a number of important "unsolved" problems have emerged as being central to the continuing development of a consistent theory of urban airshed modeling.

### 1. The Effect of Concentration Fluctuations on Turbulent Chemistry

We noted earlier that turbulent fluctuations can lead to a mean rate of reaction different than a rate based on the mean concentrations. There exists in the literature a number of theoretical studies of closure methods for terms of the form $\langle c'^2 \rangle$ and $\langle c_i' c_j' \rangle$ as arise in the second-order decay of a single reactant or the second-order reaction of two species. However, no one has yet been able to determine whether turbulent concentration fluctuations have a significant effect on atmospheric reactions in situations of practical interest. We recommend that:

a. Theoretical studies of Eulerian closure methods for simple reactions (e.g. $A + A \rightarrow$ products or $A + B \rightarrow$ products) be carried out for situations in which there exists advection, turbulent diffusion and molecular dissipation, for example, a continuous source in a uniform wind. Such studies may serve to identify regimes in which each of the processes will predominate.

**b. Experimental studies of chemical reactions in wind tunnels with well-defined turbulence be carried out to determine profiles of mean and fluctuating concentrations which can be compared with theoretical predictions.**

### 2. Parameterization of Sub-Grid Scale Transport and Reaction Effects in Grid Models

In Section B we noted that at the present time there does not exist a consistent means of including point and line sources of reacting contaminants in grid models. What is required is a means of having the source emission input into the overall airshed model reflect the transport and reaction phenomena that have taken place in the plume in the vicinity of the source. (For example, the emissions need not necessarily be allocated entirely to the grid square in which the source is located nor need the chemical composition of the source emissions function be that which was observed (or predicted) at the source.) We recommend that modeling studies be carried out on scales smaller than the urban scale, in particular, for plumes emitted from strong point and line sources. These models would then serve as "submodels" to properly introduce emissions from concentrated sources into the overall airshed model.

### 3. Sensitivity Studies with Airshed Models

In Section 4 we examined the methods of computing and and levels of uncertainty in the emissions and meteorological inputs to an airshed model. A study such as presented in Section 4 is helpful in identifying those parameters which are poorly determined and at the same time can have a significant effect on the predictions of the model. However, validation results for any urban airshed model must be accompanied by a thorough series of sensitivity runs in which each important parameter is varied over its limits and the effect on the model output is computed. At this time there do not exist any consistent sets of sensitivity runs for photochemical air pollution models. As a result, there is uncertainty as to which inputs and parameters most affect the predictions of models. There is an urgent need for such sensitivity runs, and we recommend these be carried out as soon as possible.

### 4. Experimental Needs in Model Development

We have presented in Chapters II and III an assessment of the current state of the mathematical modeling of both atmospheric photochemistry and transport and dispersion. Clearly, the development of validated models in both areas will provide valuable tools for prediction and planning. In the course of this validation several types of experimental programs will be necessary. We discuss here some of the principal experimental needs for future model development.

Kinetic mechanisms must be tested using both laboratory and actual atmospheric data. Since chemical changes in the atmosphere cannot be divorced completely from transport and diffusion effects, laboratory studies are a necessary prerequisite to validation with actual atmospheric data. Thus, Chapters IV and V are devoted to needs in relation to laboratory studies, both in smog chambers, where atmospheric processes are simulated, and in more well-defined chemical systems, in which important individual reactions are studies to determine specific rate constants and/or product distributions.

After a kinetic mechanism has been validated by comparison of its predictions with smog chamber data for a variety of conditions, then the mechanism is integrated into an airshed model that is capable of describing the dynamic transport and diffusion of pollutants in the atmosphere. As we have seen, there are several different types of airshed models, each with different restrictions, ranges of applicability and requirements imposed on a reaction kinetics model that is to be included in it. The validation of a full airshed model is clearly a more difficult undertaking than the validation of a kinetic mechanism using data from a controlled laboratory experiment. Measurements must include not only chemical compositions but also the wind flow and temperature structure of the atmosphere. And this information is, of course, needed at a substantial number of locations. Chapter VI is devoted to an examination of needs, as regards an atmospheric measurement program that will serve as the basis for model validation.

# IV. INVESTIGATION OF SPECIFIC ELEMENTARY REACTIONS AND PARTICLE GROWTH PROCESSES AFFECTING THE COURSE OF SMOG FORMATION

As we have noted in Chapter II, atmospheric contaminants participate in a large number of elementary reactions. At this time it appears that most of the important reactions that contribute to the pollutant formation in the atmosphere have been identified. Yet, our complete understanding of the mechanism of smog formation depends upon our ability to measure rate constants and to determine the mechanisms and products of several elementary reactions presently thought to be significant. In this chapter we have attempted to gather and discuss what we feel are the most important problems remaining to be solved that involve fundamental chemical kinetics.

Although our primary objective in this discussion is to identify those areas of pursuit that are most important to achieving an understanding of the pollutant-generating gas phase reactions in the atmosphere, we also examine briefly the phenomenology of gas to particle conversion, that is, the mechanism of aerosol growth. As this is a large and complex topic, one which is not well understood, we have limited the discussion to a coverage of only the key issues that require further study. We have included this cursory examination primarily to emphasize that gas phase reactions of pollutants and the formation of light-scattering aerosols are coupled processes, and thus should be investigated in a related fashion.

## A. Rate Constants and Elementary Reaction Mechanisms Requiring Further Study

The formulation of a descriptive and predictive chemical mechanism of smog formation requires identification of all the important reactions contributing to the chemical dynamics. Similarly, thorough investigation of a specific reaction is achieved only when the reaction rate constant has been carefully determined and the reaction mechanism properly specified. Due to the large number of important reactions that take place in the atmosphere, the rapid rates of many of them, and the low concentrations of most reactants (e.g. free radicals), the experimental investigation of photochemical smog formation is an enormously large and difficult task. Much has been accomplished, however, in recent years. Excellent compilations and discussions of kinetic and mechanistic studies which have been carried out can be found in Leighton (1961), Johnston et al. (1970), Altshuller and Bufalini (1971), and Demerjian et al. (1973). In this section we limit ourselves to a consideration only of those inorganic and organic reactions whose rate constants or mechanisms require further investigation in order to assess their importance with regard to the dynamics of pollutant transformations.

As will be seen in the following section the important inorganic reactions that occur in the atmosphere are reasonably well known. Approximately 15 species, mostly nitrogen-containing, participate in about 20 elementary reactions. Most of the reaction mechanisms are well understood, and the remaining problems of interest concern mainly the determination of the reaction rate constants. The set of reactions involving organic constituents, on the other hand, is extremely complex, involving hundreds of reactants. Simplified descriptions of these processes can be achieved only in that the organics can be divided into five general classes, the constituents of each class having a tendency to react similarly with a particular reactant (such as O, OH, and $O_3$. See Chapter II). Also of interest is the identification and determination of products of hydrocarbon-oxidant reactions and the measurement of rates of free radical reactions.

### 1. Inorganic Reactions

In this section we focus our attention on both the direct photolysis and thermal reactions of importance that occur in the atmosphere and that involve inorganic species. [Included among the inorganics are free radical species (e.g. O, OH, $HO_2$, NO, $NO_2$, $NO_3$), inorganic acids and acid anhydrides (e.g. $HNO_2$, $HNO_3$, $N_2O_5$), peroxides (e.g. $H_2O_2$), and other simple oxides (e.g. CO, $SO_2$).] Photodissociation reactions result in the generation of free radical species which initiate the photochemical smog process. The thermal reactions important in smog, on the other hand, are mainly chain continuing or chain terminating processes which result in the oxidation of NO, the accumulation of $O_3$, and the formation of stable products such as $HNO_3$ and $CO_2$.

#### a. Direct Photolysis Reactions

The rate constant for photodissociation of a species is normally expressed as the product of the specific absorption rate, $k_a$ , and the quantum yield, $\phi$ . The specific absorption rate is a function of the intensity and spectral distribution of the incident radiation. Rates of photodissociation reactions are usually known only with uncertainty because of the difficulty in measuring the spectral distribution of sunlight and artificial radiation sources. We defer the discussion of light intensity measurements until Chapter V.

At least three inorganic species, $NO_2$, $HNO_2$, and $H_2O_2$, will photolyze when exposed to incoming solar radiation of spectral composition typically observed at the earth's surface. Of these $NO_2$ dissociation is clearly the most important. At this point the significance of $HNO_2$ decomposition and the effect of this reaction on smog dynamics has not been clearly established, largely because $HNO_2$ is rarely, if ever, measured either in the atmosphere or in smog chambers. Probably the least important contributor to smog formation of the three reactions mentioned above is the photolysis of $H_2O_2$. $H_2O_2$ does not photolyze readily and, because it is produced late in the smog formation cycle, has little effect on the overall chemical dynamics. (Ozone will also photolyze slowly. Because $O_3$ does not accumulate until the $NO_2$ maximum has been reached, this reaction would not be important until late afternoon, if at all.)

### (1) $NO_2$

$NO_2$ is the primary energy absorber of those pollutants present in the atmosphere. The photodissociation of $NO_2$,

$$NO_2 + h\nu \rightarrow NO + O$$

has long been recognized as the most important chain initiation reaction in smog formation. We shall discuss the experimental measurement of the photolysis rate constant for this reaction in Chapter V.A.

### (2) $HNO_2$

A second energy-absorbing species thought to be present in polluted air and in smog chambers is nitrous acid. (In Chapter IV.A.1.b.(3). We discuss the chemistry of nitrous acid formation.) At wavelengths greater than 3000 Å two primary photodissociation reactions are possible (Leighton, 1961):

$$HONO + h\nu \rightarrow OH + NO - (\sim 60\text{kcal})$$

$$HONO + h\nu \rightarrow H + NO_2 - (\sim 80\text{kcal})$$

The rate of photolysis of $HNO_2$ is about 1/10 that of $NO_2$. (Johnston et al., 1970.)

The importance of $HNO_2$ in initiating smog formation is a consequence of the high reactivity of the OH radical with hydrocarbons.* In the case of the second reaction the H atom combines rapidly with $O_2$ to form an $HO_2$ radical. The $HO_2$ radicals may then react with NO or another $HO_2$ radical, thereby initiating reactions which ultimately lead to the formation of OH radicals.

$$HO_2 + NO \rightarrow OH + NO_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu \rightarrow 2OH$$

Although measurements of atmospheric $HNO_2$ concentrations have not been reported, we can estimate roughly the equilibrium concentration of $HNO_2$ that would be established under typical atmospheric conditions. Using equilibrium constants determined by Wayne and Yost (1951) and concentrations of NO (0.2 ppm), $NO_2$ (0.1 ppm) and humidity (63% at 25°C) which are typically observed in Los Angeles just before sunrise, we estimate the equilibrium concentration of $HNO_2$ to be about 0.026 ppm or about 1/4 of the $NO_2$ concentration. At these low concentrations $HNO_2$ will form at a rate of about 0.10 ppm/hour. (If the concentration of NO were 0.40 ppm and $NO_2$ were 0.20 ppm, the rate of nitrous acid production would rise to about 0.40 ppm/hour, and the equilibrium concentration would be about 0.05 ppm). Thus, nitrous acid may well be an important source of free radicals early in the morning in a polluted atmosphere.

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* Hydroxyl radicals react about fifty times more rapidly with alkanes, and about 10 times more rapidly with olefins, than do oxygen atoms.

### (3) $\underline{H_2O_2}$

Recent evidence suggests that hydrogen peroxide may exist in significant concentrations in polluted air. Bufalini et al. (1972) measured 0.18 ppm of $H_2O_2$ under severe smog conditions in Riverside, California and they suggested that $H_2O_2$ forms primarily as a result of $HO_2$-$HO_2$ recombination. However, hydrogen peroxide is probably not a major factor in hydrocarbon oxidation ( by production of OH radicals) for the following reasons:

1. Under equivalent irradiation conditions, its photodissociation rate is only 1/250 that of $NO_2$. (Leighton, 1961.)
2. Maximum concentrations of $H_2O_2$ observed in the laboratory and the atmosphere are much less than the corresponding maximum concentrations of $NO_2$ (Bufalini et al., 1972).

3. $H_2O_2$ forms at the fastest rate after the $NO_2$ peak, coincident with the onset of oxidant formation and after much of the hydrocarbon has been oxidized.

4. $H_2O_2$ actually serves as a sink for $HO_2$ radicals, since the subsequent production of OH radicals from photolysis is slow.

For these reasons it is probably important to measure the concentration of $H_2O_2$ only for the purposes of modeling the post-$NO_2$-peak smog formation behavior.

## b. Thermal Reactions

When a mixture of $NO_2$, NO, CO, $SO_2$, and $H_2O$ is irradiated in air, a large number of "secondary" reactions can occur subsequent to $NO_2$ photolysis. These "secondary" reactions are thermal rather than photolytic in nature, since the energy contained in the reactants and that produced by their collision, rather than light energy, drives the reaction. In this section we discuss the important inorganic reactions that occur in the atmosphere, examining in particular the formation of the inorganic acids, $HNO_3$ and $HNO_2$, and the oxidation of NO, CO, and $SO_2$. Before doing this, however, we briefly discuss the effect of temperature on the rate of the homogeneous reactions contributing to smog formation.

It has been observed by several investigators that increasing the operating temperature of a smog chamber results in an increase in the photooxidation rates of hydrocarbons and in the ozone levels attained. (Early literature on this subject has been reviewed by Altshuller and Bufalini (1965).) This is the effect one would expect of reactions having substantial activation energies. However, most of the inorganic and organic reactions contributing to smog formation for which activation energies $(E_A)$ have been determined have values of $E_A$ less than 5 kcal. (See Johnston et al. (1970).) For instance, the $NO$-$O_3$ reaction (IV.A.1.b.(1)), which contributes substantially to $NO$ and $O_3$ loss rates and the $NO_2$ formation rate, has an activation energy of 2.5 kcal. Increasing the temperature from 77°F to 95°F (25°C to 35°C) increases the rate constant from 29.4 $ppm^{-1}min^{-1}$ to 33.8 $ppm^{-1}min^{-1}$, (a 15% change, which by itself should have little effect on the time to the $NO_2$ peak or the ozone level attained). The activation energy of the $NO_2$-$O_3$ reaction (IV .A.1.b.(1)), on the other hand, is 7.0 kcal, and a 10°C increase in temperature results in a 46% increase in the rate constant. The only reaction of those listed in Johnston et al. (1970) having a high activation energy is the reaction

$$N_2O_5 \rightarrow NO_2 + NO_3$$

which has an activation energy of 21 kcal.

To determine the effect of temperature on the rate of smog formation it will be necessary to incorporate the thermal dependence of the various rate constants into kinetic mechanisms. However, activation energies have not yet been determined for all the reactions thought to be important in smog formation (for example, the $HNO_2$ formation and $HO_2$-NO reactions). Thus, we recommend that an effort be made to obtain the data needed to establish k versus T relationships.

(1) Reactions of $O_3$ With NO and $NO_2$

Ozone, which forms as a product of $NO_2$ photolysis by the reactions,

$$NO_2 + h\nu \xrightarrow{k_1} NO + O$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M \quad M = \text{third body}$$

is destroyed rapidly in the presence of NO by the reaction

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2$$

As the overall smog formation process proceeds, NO is depleted and $NO_2$ and $O_3$ accumulate. When $NO_2$ and $O_3$ reach sufficiently high concentration levels, the reaction

$$O_3 + NO_2 \xrightarrow{k_4} NO_3 + O_2$$

becomes more important than the $O_3$-NO reaction.

Two determinations have been made of the rate constant for the $O_3$-$NO_2$ reaction, $k_4$ : 0.106 $ppm^{-1}min^{-1}$ by Johnston and Yost (1949) and 0.0485 $ppm^{-1}min^{-1}$ by Ford et al. (1957). The earlier measurement was made at partial pressures of $NO_2$ between 0.001 and 0.01 atmospheres--pressures that are much higher than those typically observed. The latter determination was made at concentrations of $NO_2$ and $O_3$ below 1 ppm. In that study $O_3$ and $NO_2$ entered a flow reactor at known concentrations. The effluent stream was analyzed continuously for $NO_2$ using a wet method similar to the Saltzman method (see Chapter V), while ozone was determined *in situ* by ultraviolet photometry. The accuracy of the rate constant determined by Ford et al. is affected by several factors, including the constancy of the inlet reactant concentrations, the completeness of mixing, and the accuracy of the $NO_2$ and $O_3$ measurements. Because of the possible sources of error and the lack of agreement between the two experimental determinations of $k_4$, it would be worthwhile to re-evaluate this rate constant.*

### (2) The Chemistry of $NO_3$, $N_2O_5$, and $HNO_3$

Any $NO_3$ formed by reaction 4 before the $NO_2$ peak will react rapidly with NO to regenerate $NO_2$ by the reaction,

$$NO_3 + NO \xrightarrow{k_5} 2NO_2$$

After the $NO_2$ peak, a time after which NO has reached low levels, $NO_3$ will react primarily with $NO_2$, presumably leading to an equilibrium concentration of $N_2O_5$.

$$NO_3 + NO_2 \underset{k_7}{\overset{k_6}{\rightleftarrows}} N_2O_5$$

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* Eschenroeder (1972) found it necessary, in validating a photochemical mechanism proposed by him to use a value of $k_4 = 0.005$ ppm $^{-1}$min$^{-1}$, while Hecht and Seinfeld (1972) used a value of $0.006$ ppm$^{-1}$min$^{-1}$. Employing values closer to the lowest experimental value of $k_4$ resulted in a reduced maximum $NO_2$ concentration, in much more rapid disappearance of $NO_2$, and in greatly (60%) reduced ozone levels. Because both mechanisms are subject to a large amount of uncertainty, there is no assurance that values of $k_4$ necessary to simulate smog chamber data are, indeed, closer to reality. Nonetheless, the modeling results serve to raise questions about validity of $k_4$ determinations carried out to date.

In the presence of water, however, $N_2O_5$ can hydrolyze to form nitric acid.

$$N_2O_5 + H_2O \xrightarrow{k_8} 2HNO_3$$

Smith (1947) has observed that $HNO_3$ reacts with NO by a process having the following overall stoichiometry:

$$2HNO_3 + NO \rightarrow 3NO_2 + H_2O$$

A reaction sequence that may possibly account for this (Johnston et al., 1955; Gray et al., 1972) is

$$HNO_3 + NO \rightarrow HNO_2 + NO_2$$

$$HNO_3 + HNO_2 \rightarrow 2NO_2 + H_2O$$

The magnitudes of the rate constants and the effect of surfaces on the rates of these two elementary reactions have not yet been established quantitatively. But, in view of the large amount of $HNO_3$ which forms in smog, such an investigation would be valuable.

Beyond those two reactions, $HNO_3$ is not thought to enter into any reactions of importance with the other pollutants present in a smog chamber. And, while the acid will photodissociate at shorter wavelengths, the photolysis does not proceed at wavelengths present in smog chambers (Berces and Forgeteg, 1970a, 1970b). (In the atmosphere, however, $HNO_3$ can read rapidly with $NH_3$ to form $NH_4NO_3$, a constituent of atmospheric aerosols.)

Although nitric acid has been found on the walls of smog chambers (Gay and Bufalini, 1971), the rate of hydrolysis of $N_2O_5$ has not been established, and it is not yet certain that reaction 8 is the primary source of $HNO_3$. (An alternate source of $HNO_3$ is the reaction of OH and $NO_2$.) Wilson (1972) has charged a humidified reactor with $N_2O_5$ and observed that the oxide disappears very slowly. This behavior suggests that gas phase hydrolysis of $N_2O_5$ is similarly very slow. Thus, the presence of a third body covered with at least a monolayer of water may be required to promote the hydrolysis reaction.

If the hydrolysis of $N_2O_5$ is slow, one could reasonably expect a large steady state concentration of $N_2O_5$ to be present in smog chambers. Wilson (1972) carried out an experiment in which he irradiated a hydrocarbon-$NO_x$ mixture until the NO had been oxidized and the $O_3$ maximum reached. He then extinguished the lights and injected NO into the system in an amount in excess of that needed to destroy all ozone present. Subsequently, he observed that the remaining NO was slowly oxidized to $NO_2$. A possible explanation for this observed behavior is that $N_2O_5$ had accumulated during the HC-$NO_x$ irradiation and then reacted with the excess NO via reactions 5 and 7. Were this the case, one would expect to observe three parts of $NO_2$ formed for each part of NO consumed. Note that this is the same stoichiometry as that observed for the $HNO_3$-NO oxidation process just described.

In summary, the atmospheric chemistry of $N_2O_5$ requires further investigation. In particular, it will be important to measure the gas phase rate constant for the $N_2O_5$-$H_2O$ reaction, the rate of the $HNO_3$-NO reaction, and the steady state concentration of $N_2O_5$ in a dry system.

### (3) The Chemistry of $HNO_2$

The photolysis and estimated equilibrium concentration of nitrous acid in the atmosphere have been discussed earlier in this chapter. We briefly examine here the reactions which produce $HNO_2$. Nitrous acid is known to form in *aqueous solution* by the reactions

$$NO + NO_2 \underset{k_{10}}{\overset{k_9}{\rightleftarrows}} N_2O_3$$

$$N_2O_3 + H_2O \xrightarrow{k_{11}} 2HNO_2$$

Grätzel et al. (1970) have studied this system and have determined the pseudo-first order rate constant for the hydrolysis of of $N_2O_3$ to be $3.18 \times 10^4 \text{min}^{-1}$. Nitrous acid is presumed to form in the atmosphere by the same mechanism, although the homogeneous gas phase hydrolysis of $N_2O_3$ may be very slow, as is the case for $N_2O_5$. Wayne and Yost (1951) studied the third order gas phase reaction,

$$NO + NO_2 + H_2O \rightarrow 2HNO_2 \quad ,$$

obtaining a rate constant of $4.3 \times 10^{-6} \text{ppm}^{-2}$ $\text{min}^{-1}$ for the reaction. Westberg (1972) has questioned the accuracy of this determination, based on thermodynamic considerations.

In the ambient system nitrous acid can form at night through the hydrolysis of $N_2O_3$, so that an equilibrium concentration of $N_2O_3$ may be reached by sunrise. Hydrolysis of $N_2O_3$ is probably also a favored reaction on wet surfaces, such as on particles or walls. As such, it very likely occurs on surfaces in smog chambers. Because of the potentially important role of $HNO_2$ in atmospheric photooxidation reactions, we recommend that the rate of formation of this species in the gas phase be carefully assessed.

### (4) Reactions of OH with NO and $NO_2$

From our discussion in Chapter II, it should be clear that OH is the most important oxidizer of hydrocarbons in smog. Thus, any reactions which affect the concentration of OH can result in a pronounced change in the rate at which smog is observed to form. Two such reactions are the termination reactions of OH with $NO_2$ and NO.

$$OH + NO_2 \xrightarrow{k_{12}} HNO_3$$

$$OH + NO + M \xrightarrow{k_{13}} HNO_2 + M$$

Morley and Smith (1972) have determined $k_{12}$ for conditions between 20 and 300 torr, conditions which they have shown exhibit a transition between third and second order kinetics. Based on their data they have estimated 15000 $ppm^{-1}min^{-1}$ to be the lower limit of the rate constant at $300^oK$ and atmospheric pressure. Using a separate technique Simonaitis and Heicklen (1972) have determined $k_{12}$ to be 13,000 $ppm^{-1}min^{-1}$ at $300^oK$ and atmospheric pressure. There have been no determinations of $k_{13}$ at pressures greater than 30 torr (Morley and Smith,1972). However, Demerjian et al. (1973) have estimated

$k_{13}$ to be equal to $0.8(k_{12})$ at atmospheric pressure. Because of the importance of OH in the smog formation process, an effort should be made to confirm this estimate experimentally.

## (5) Oxidation of NO by $HO_2$

Until recently there has been little direct evidence to substantiate the hypothesis that $HO_2$ is an important oxidizer of NO in the smog formation process. Wilson and Ward (1970) have observed that irradiation of NO (~1 ppm) in the presence of large amounts of CO (~500 ppm) in air results in the complete oxidation of NO to $NO_2$ and the formation of $O_3$. The mechanism generally assumed to explain this observation is as follows. Water in the air reacts with NO and traces of $NO_2$ to form nitrous acid, which subsequently photolyzes to form OH radicals. The following reactions then occur:

$$OH + CO \xrightarrow{k_{14}} CO_2 + H$$

$$H + O_2 + M \xrightarrow{k_{15}} HO_2 + M$$

$$HO_2 + NO \xrightarrow{k_{16}} OH + NO_2$$

The rate constant for reaction 14 is now well established (see the next section), and the combination of H with $O_2$ is very fast. Apparently the first reported value for $k_{16}$ was that determined by Johnston et al. (1970), 3 $ppm^{-1}min^{-1}$. Recently, however, Davis et al. (1972) have experimentally established $k_{14}$ as being 700 $ppm^{-1}min^{-1}$. The earlier low value is probably incorrect, since with such a value the oxidation of NO in the presence of CO and light cannot be satisfactorily explained. We recommend that the value determined by Davis be used in subsequent calculations.

### (6) Oxidation of CO

Carbon monoxide has been shown to accelerate the oxidation of NO to $NO_2$ when present in concentrations of 100 ppm or more (Westberg et al., 1971). The effect of CO is explained by reactions 14-16; accordingly, the first step in the chain, the oxidation of CO by OH (reaction 14), has received a great deal of attention. Demerjian et al. (1973) have averaged the experimental determinations of $k_{14}$ made by several investigators and have obtained a value of 250 $ppm^{-1}min^{-1}$. Because ambient concentrations of CO are well below 100 ppm, often on the order of 5-30 ppm, CO probably has little effect on smog formation (Dodge and Bufalini,1972).

A simplified example may be used to illustrate the acceleration in the rate of oxidation of NO in the presence of CO due to an increase in the ratio of the rate of radical formation to the rate of radical termination. The four most important reactions in smog involving OH are

$OH + NO_2 \rightarrow HNO_3$ $k = 15{,}000\ ppm^{-1}min^{-1}$

$OH + NO \rightarrow HNO_2$ $k = 12{,}000\ ppm^{-1}min^{-1}$

$OH + HC \xrightarrow{O_2} 1RO_2$ $k = 25{,}000\ ppm^{-1}min^{-1}$ for propylene

$OH + CO \xrightarrow{O_2} 1HO_2$ $k = 250\ ppm^{-1}min^{-1}$

If propylene, NO, and $NO_2$ are all present at a concentration of 1 ppm,

$$R = \frac{\text{The rate of radical formation}}{\text{The rate of radical termination}}$$

$$= \frac{25000}{15000+12000+25000} \approx 0.48$$

If 100 ppm CO are added to the system,

$$R = \frac{25000+25000}{15000+12000+25000+25000} \approx 0.65$$

Thus, the addition of 100 ppm of CO to this system results in a 35% increase in the ratio of the rate of radical formation to the rate of radical termination.

The effect of CO is even more striking in a system containing a hydrocarbon of lower reactivity, such as n-butane, for which the OH-n-butane rate constant is 3800 $ppm^{-1}min^{-1}$. In this case, if (n-butane) = (NO) = ($NO_2$) = 1ppm,

$$R = \frac{3800}{15000+12000+3800} = 0.12$$

Upon addition of 100 ppm CO, R increases to

$$R = \frac{3800+25000}{15000+12000+3800+25000} = 0.52$$

The ratio of the rate of radical formation to the rate of termination has, therefore, increased fourfold upon addition of the CO. Thus, the effect of high concentration of CO on the rate of smog formation may be expected to be proportionately greater for systems containing hydrocarbons of low reactivity than for those containing hydrocarbons of high reactivity.

Recently, there has been some interest in the possible oxidation of CO by $HO_2$,

$$HO_2 + CO \xrightarrow{k_{17}} OH + CO_2$$

Westenberg (1972) has determined experimentally the ratio of the rate of this reaction to that of $HO_2$ and H. In particular, he estimated that the $HO_2$-CO reaction is probably very fast, with a rate constant on the order of $8.8 \times 10^4 ppm^{-1} min^{-1}$. If this is the case, the $HO_2$-CO reaction has the effect of raising the OH concentration predicted by kinetic mechanisms. Consequently, the rate of loss of hydrocarbon through reaction with OH and the rate of generation of NO-oxidizing free radicals is also increased. The value Westenberg obtained for the $HO_2$-CO rate constant, however, depends crucially on the kinetic mechanism upon which the data analysis was based. In his analysis he omitted from the mechanism the reaction between OH and $HO_2$,

$$OH + HO_2 \rightarrow H_2O + O_2$$

a reaction which must be of some importance. This omission resulted in the overestimation of the $HO_2$-CO rate constant (Dodge, 1973). Davis et al. (1972), too, have recently completed a study of the $HO_2$-CO reaction and have obtained a value for the rate constant of less than $8 \times 10^{-5} ppm^{-1} min^{-1}$. Thus, it now appears that reaction 17 is too slow to be of importance in smog formation.

### (7) Oxidation of $SO_2$

The oxidation of $SO_2$ in an atmosphere containing oxides of nitrogen and hydrocarbons and in the presence of sunlight is an extremely complicated process, one which is not fully understood. The following reactions have been studied thus far:

1) the direct photolysis and quenching of $SO_2$
2) the reaction of $SO_2$ in its excited states with $O_2$ and
3) the oxidation of $SO_2$ by O and $O_3$

If these were the only $SO_2$ oxidation reactions occurring, we would expect a maximum rate of disappearance of $SO_2$ in the atmosphere of about 2% per hour, a value which is considerably lower than that observed in an atmosphere containing $NO_x$ and hydrocarbons. We shall not endeavor to examine photochemical oxidation reactions involving $SO_2$ in detail here, as a thorough review of these reactions has recently been presented by Bufalini (1971). Rather, we will restrict ourselves to a discussion of reactions which have recently been postulated to explain the atmospheric photochemistry of $SO_2$.

Cox and Penkett (1971) have reported that $SO_2$ is oxidized by a product of the $O_3$-olefin reaction, presumably the so-called "zwitterion".

$$R\overset{\oplus}{C}HOO^{\ominus} + SO_2 \rightarrow SO_3 + RCHO$$

Since the disappearance rate of $SO_2$ in a smog chamber experiment increases during the period of ozone accumulation (Wilson and Levy (1970), this reaction is plausible. The zwitterion, a peroxide characterized by strong charge separation, should be an effective oxidizing agent. Wilson et al. (1972) have suggested that $SO_2$may be oxidized by either $NO_3$ or $N_2O_5$, or both:

$$NO_3 + SO_2 \rightarrow SO_3 + NO_2$$

$$N_2O_5 + SO_2 \rightarrow SO_3 + 2NO_2$$

This hypothesis is of interest in that it implies that only $O_3$ and $NO_2$, the precursors of $NO_3$ and $N_2O_5$, are needed to oxidize $SO_2$. While Wilson et al. (1972) made their observations for a system also containing hydrocarbons, it would be interesting to perform a "dark" reaction for a system of $NO_2$, $O_3$, and $SO_2$ in air. Carrying out the reaction in the dark would prevent the formation of O atoms, which are known to oxidize $SO_2$.

$$O + SO_2 + M \rightarrow SO_3 + M$$

It has long been speculated that peroxy radicals ($HO_2$, $RO_2$, etc.) might be important in the photochemical oxidation of $SO_2$. However, this now seems to be unlikely. Recent preliminary results obtained by Davis et al. (1972) indicate that the $HO_2$-$SO_2$ reaction is very slow, having a rate constant of only about 0.8 $ppm^{-1}min^{-1}$.

c. Summary

In the foregoing presentation we have discussed several inorganic reactions of importance, or possible importance, in smog formation which require further investigations and understanding. Many of these reactions have already been studied in detail; however, some may require a careful re-determination of the rate constants. Specifically, we recommend that:

1) The rates of photodissociation of $NO_2$, $HNO_2$, and $H_2O_2$ be measured carefully in both smog chambers and the atmosphere. Additionally, the concentrations of $HNO_2$ and $H_2O_2$ should be monitored continuously, as is now done for $NO_2$, so that their importance as free radical initiators in the smog system can be evaluated.

2) The $O_3$-$NO_2$ rate constant be re-determined. The magnitude of this rate constant strongly affects the $NO_2$ disappearance rate and peak ozone levels predicted by smog mechanisms.

3) The rate of reaction of $N_2O_5$ and $H_2O$ in the gas phase be measured. Nitrogen balances in smog chambers have been notoriously poor, a difficulty that is attributable to the formation of $HNO_3$. A point of interest in the development and validation of kinetic mechanisms is to establish whether $HNO_3$ forms in the gas phase and is transported to surfaces, or whether the hydrolysis takes place predominantly on walls and particles.

4) The rate of formation of $HNO_2$ by the hydrolysis of $N_2O_3$ be re-determined in the gas phase. Again, $HNO_2$ should be measured routinely in smog chambers and the atmosphere if its formation rate is significant.

5) The rate of reaction of OH and NO be determined. Such knowledge is needed if we are to predict accurately the rate of hydrocarbon oxidation by OH up to the time of the $NO_2$ peak.

6) The rates at which $NO_3$, $N_2O_5$, zwitterions, and free radicals react with $SO_2$ be determined. This information will aid in explaining the observed rates of $SO_2$ oxidation in photochemical smog formation.

## 2. Organic Reactions

Although the irradiation of a system containing NO, CO, $H_2O$, and air will result in the oxidation of NO and production of ozone, the addition of any of several organic species to the system substantially accelerates the photo-oxidation process. Organics that will enhance the oxidation rate include olefins, aldehydes, ketones, most paraffins and aromatics, and the longer chain acetylenes. These species enter the atmosphere in several ways.

1) Auto exhaust contains large amounts of unburned and partially burned gasoline.
2) The filling of gas tanks displaces air saturated with gasoline into the atmosphere.
3) Organic solvents used in metal working plants, dry cleaning, and as carriers for paints evaporate into the air.
4) Organic products escape to the atmosphere from chemical manufacturing plants such as petroleum refineries.

The contribution from motor vehicles is the highest, however, being about 66% of the total organics and 86% of the reactive organics found in the Los Angeles atmosphere.

In a study of the effect of varying engine operating conditions on exhaust composition, Jackson (1966) found that ethylene, propylene, and butenes constituted approximately 34% of the hydrocarbons found in exhaust, toluene and xylenes about 10%, and unreactive hydrocarbons (methane, ethane, propane, acetylene, and benzene) about 24%. Eccleston and Hurn (1970) have measured the composition of exhaust emissions from eight automobiles in an effort to determine the effect of switching from leaded to unleaded gasolines. The average emissions from cars using regular leaded gasoline were:

| | |
|---|---|
| 38.34% | paraffins |
| 36.45% | olefins |
| 13.34% | aromatics |
| 1.41% | oxygenates |
| 10.61% | acetylenes |

Running the cars on a regular, low olefin fuel resulted in a large increase in the aromatic content and a moderate decrease in the olefinic content:

| | |
|---|---|
| 34.02% | paraffins |
| 28.75% | olefins |
| 25.95% | aromatics |
| 1.66% | oxygenates |
| 9.63% | acetylenes |

Exhaust analysis of the cars run on an unleaded, high olefin fuel showed a moderate increase in aromatic emissions and an almost equal decrease in olefinic emissions, when compared with emissions measured using regular leaded fuel:

| | |
|---|---|
| 35.92% | paraffins |
| 31.34% | olefins |
| 21.06% | aromatics |
| 1.86% | oxygenates |
| 10.13% | acetylenes |

Thus, switching from leaded to unleaded gasoline resulted in an increase in combined olefinic and aromatic emissions and reduced paraffinic emissions. Because olefins and aromatics are, as a class, more reactive than are paraffins with respect to the oxidation of NO, removal of lead from gasoline will probably result in an atmospheric hydrocarbon mix of increased photochemical reactivity.

In 1967 Altshuller et al. (1971) measured the hydrocarbon composition of the atmosphere at two locations in the Los Angeles Basin. They found that atmospheric organics consist of about:

| | |
|---|---|
| 53% | paraffins (excluding methane) |
| 16% | olefins |
| 20% | alkyl benzenes |
| 11% | acetylene |

Considerable effort has been expended in the past to study the reactions of paraffins and olefins with oxidants. Yet, Altshuller's study shows that aromatics constitute a significant percentage of the total hydrocarbon in the Los Angeles Basin. Altshuller et al. (1971) found that toluene and m-xylene are two of the ten individual hydrocarbons present in the greatest concentrations and that these two hydrocarbons constitute about half of the alkylbenzene fraction. As will become apparent in the discussion that follows, the elementary reaction mechanism for the oxidation of aromatics in the atmosphere is poorly understood. In view of the high aromatic content of the atmosphere and of auto exhaust, this lack of understanding stands as an impediment to progress in the kinetic modeling of photochemical smog.

In this section we begin by examining the mechanism and products of the oxidation of each class of hydrocarbons (paraffins, olefins, aromatics, and acetylenes) by O, OH, $O_3$, and $^1O_2$. We then discuss the reactions of aldehydes and ketones that can occur in the atmosphere. Finally, we describe the reactions of free radicals, the products of hydrocarbon oxidation reactions. Some of this material to be presented has been discussed previously (in Chapter II) in explicating the development of generalized kinetic mechanisms. However, particular attention will be given here to those elementary reactions whose mechanisms require further investigation.

### a. The Mechanisms of Oxidation of Hydrocarbons in Smog

Elucidation of the mechanisms of hydrocarbon-oxidant reactions that contribute to smog formation has proven to be an arduous task. The low concentrations of the reactants, the typically rapid rates of reaction, and the short life-times and low concentrations of the products of the primary oxidation have, in general, precluded definitive experimental investigations. In this section we discuss the reactions of the four most common classes of hydrocarbons (paraffins, olefins, aromatics, and acetylenes) with O, OH, and $O_3$, the oxidants thought to be the most important in smog formation. We also briefly examine the role of singlet oxygen in hydrocarbon oxidations. We will not tabulate the rate constants of the hydrocarbon-oxidant reactions here, since this has been done recently by Johnston et al. (1970) and Demerjian et al. (1973). However, where omissions have been made in their tabulations, or where new data have become available, we will so note.

#### (1) O Atom Oxidation Reactions

Oxygen atoms form as a result of $NO_2$ photolysis and are generally thought to be the species that initiate the reactions leading to pollutant formation in smog chambers. However, while O atoms react rapidly with olefins, reactions of aromatics and acetylenes with O atoms proceed slowly, at rates about one to two orders of magnitude slower than for olefins.

(a) Reactions with Paraffins

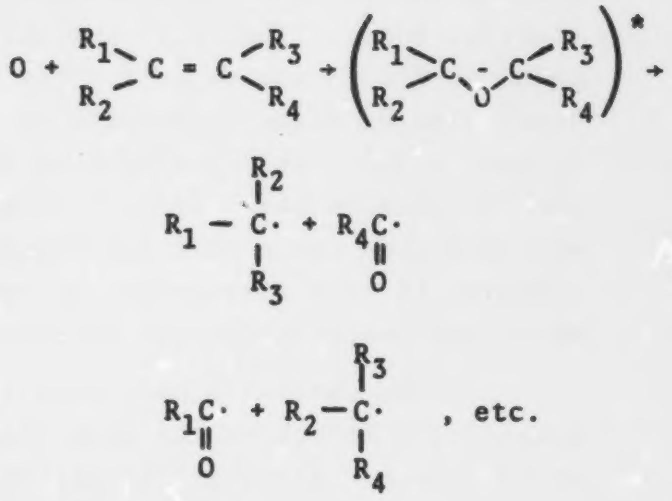
The reaction of O with paraffins probably results in the abstraction of a H atom (Leighton, 1961 )

$$RH + O \rightarrow R\cdot + OH$$

The result of the reaction then is free radical branching to an alkyl radical and an OH radical.

(b) Reactions with Olefins

Oxygen atoms generally add to olefins forming an excited epoxide, which then decomposes to an alkyl and an acyl radical. (Leighton, 1961)

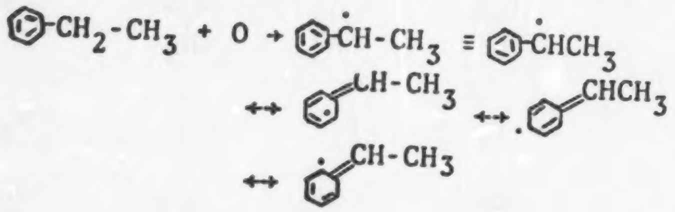


This reaction, thus, results in the formation of two free radicals.

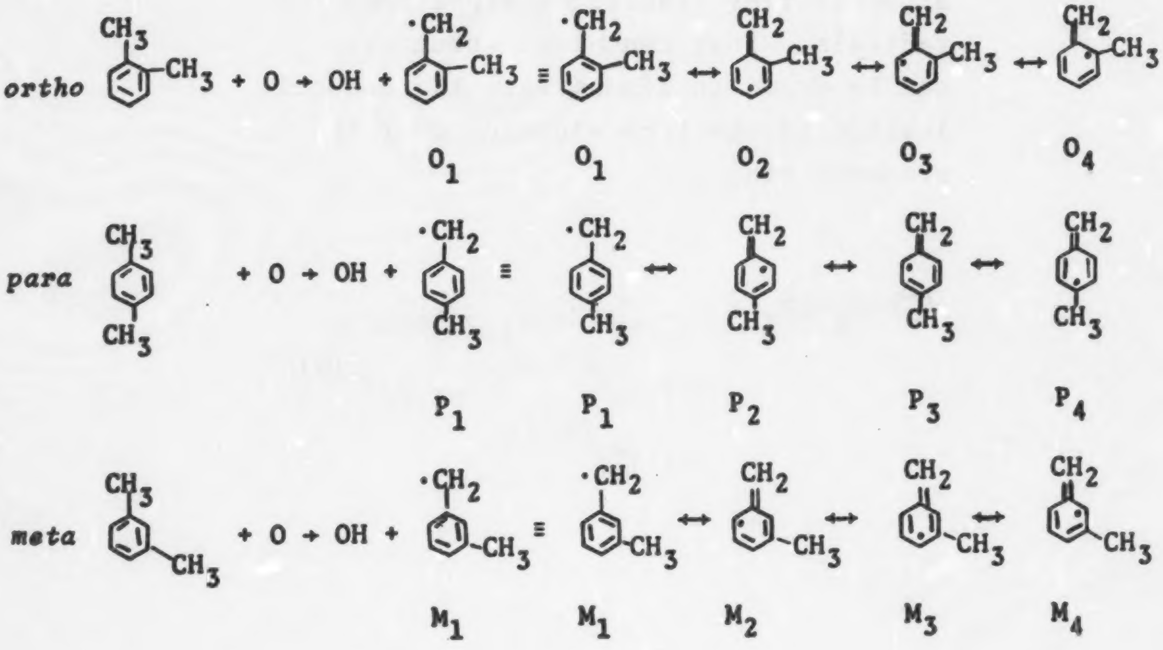
### (c) Reactions with Aromatics

The mechanism for O atom attack on aromatics is not yet known. Among the products that have been observed from the reaction chain initiated by O attack on aromatics are peroxides, acids, and alcohols (Eventova and Pryktova, 1960). The reaction of O with benzene is very slow. With mono-substituted aromatics O might attack either the alkyl side chain (as it would a paraffin) or the ring. There is little evidence to indicate which of the two mechanisms predominates, but studies of toluene and $NO_x$ in smog chambers have led to the observation of benzaldehyde and peroxybenzoylnitrate as products (Heuss and Glasson, 1968). The fact that these products are formed suggests that at least some oxidants react with toluene in such a way that chain opening does not directly result. Since O attack on an alkyl side chain of a substituted aromatic is such a reaction, we speculate about the reaction in some detail.

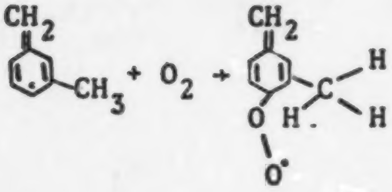
In the case of a mono-substituted aromatic, O attack on the side chain would probably occur at the carbon atom in the alpha position relative to the ring location. The carbon-hydrogen bond at that position has an unusually low bond dissociation energy, as the aromatic ring stabilizes alpha free radicals. Four canonical structures can be drawn to demonstrate the delocalization of the free electron over the aromatic ring.



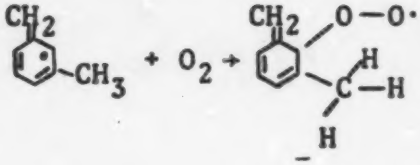
Among the dialkyl substituted aromatics one might expect the meta-substituted isomers to be the most reactive with respect to smog formation. Consider the reactions of ortho, meta, and para xylene. The initial hydrogen abstraction is identical in each case, a radical forming for which four delocalization structures can be written:


ortho
+ O → OH +
$O_1$ $O_1$ $O_2$ $O_3$ $O_4$
para
+ O → OH +
$P_1$ $P_1$ $P_2$ $P_3$ $P_4$
meta
+ O → OH +
$M_1$ $M_1$ $M_2$ $M_3$ $M_4$

Thus, the initial product is a very stable free radical. The addition of molecular oxygen to the ortho or para free radicals at any of the four positions, or to the meta free radical in positions $M_1$ or $M_2$, results in a loss of free radical delocalization, that is, only one canonical structure can be written. Thus, the peroxy radical is less stable than the alkyl radical, and there is a tendency for the radical to split off the $O_2$ again. Positions $M_3$ and $M_4$ of the meta free radical are special cases, however, with the addition of molecular oxygen favored at these sites. Upon addition of oxygen the radical takes the form,

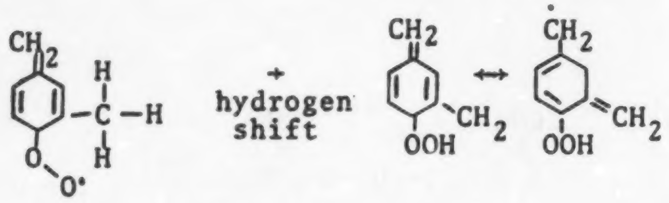


$M_3$ $M'_3$

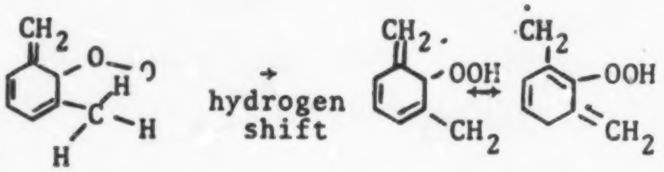


$M_4$ $M'_4$

with the free electron localizing on the outer oxygen. Note that in each case the two oxygens, two carbons on the ring, and the carbon and a hydrogen of the methyl group form a six-membered ring. Given the proximity of these various groups and atoms to each other, transfer of an H atom from the methyl group to the peroxy radical is highly likely. Thus we would expect the following reaction to occur:


CH2
H
C
H
H
O
O·
hydrogen shift
CH2
CH2
OOH
CH2
CH2
OOH

$M_3'$ $M_3''$


CH2
O
O
H
C
H
H
hydrogen shift
CH2·
OOH
CH2
·CH2
OOH
CH2

$M_4'$ $M_4''$

In each case radicals form ($M''_3$ and $M''_4$) which create the opportunity for an additional degree of delocalization to occur. Thus, reactions involving the meta radical differ from these involving the ortho and para radicals in that oxidation is energetically favorable at more than one position on the ring. In the presence of sunlight and photochemical oxidants the oxidation will probably result in complete fragmentation of the radicals $M''_3$ and $M''_4$. However, it is not possible at this time to specify the mode or degree of branching.

From the foregoing discussion it is apparent that little is known about the mechanism of O atom oxidation of aromatics. In addition, we should note that rate constants for O attack on aromatics in the gas phase have been measured only for benzene and toluene. Thus, as a serious gap exists in our understanding and knowledge of the O aromatic reaction system, we strongly recommend that

(1) rate constants for O attack on important aromatics other than benzene and toluene (such as o, m, and p xylene, ethylbenzene, 1,2,4-trimethylbenzene) be measured

and (2) the mechanism of the O-aromatic reaction and the radicals formed either directly as products or as the result of fragmentation of the initial products in the reaction be determined.

## (d) Reactions with Acetylene

The reactions of O with acetylene have been studied in flames (Fenimore and Jones, 1963) over a temperature range of 970° to 1660°K and in shock tubes (Glass et al., 1965), also at very high temperatures. Possible products of the reaction suggested by these investigators include

$$\begin{array}{lcll} & \nearrow & H + HC_2O & \text{Fenimore and Jones} \\ O + C_2H_2 & \rightarrow & CH_2 + CO & \text{Fenimore and Jones} \\ & \searrow & C_2H + OH & \text{Glass et al.} \end{array}$$

Fenimore and Jones have determined the rate constant to be between $2.45 \times 10^4$ and $4.90 \times 10^4$ $ppm^{-1}min^{-1}$, with little temperature dependence over the range 970-1660°K. At room temperature the rate constant may be slower than that for the O-olefin reactions and faster than that for the O-paraffin reactions (Leighton, 1961), but apparently it has not been conclusively measured. It is desirable that the mechanism and rate of O attack on acetylene be determined, since acetylenes constitute a significant portion of atmospheric hydrocarbons.

### (2) OH Radical Oxidation Reactions

Hydroxyl radicals enter the photochemical smog system as a result of $HNO_2$ photolysis and as products of the degradation reactions of free radicals such as those that follow the O-hydrocarbon reactions.

$$HNO_2 + h\nu \rightarrow OH + NO$$

$$\begin{tikzcd}
CH_3 + O_2 \arrow[r] & CH_3OO \arrow[r, "NO"] & CH_3O + \dot{N}O_2 \arrow[d, "O_2"] \\
& & HO_2 + HCHO \arrow[d, "NO"] \\
& & OH + NO_2
\end{tikzcd}$$

Reactions of OH with hydrocarbons are very similar to those of O, with two exceptions:

(1) the reactions of OH with a given hydrocarbon are generally very much faster than those of O, and

(2) hydrogen abstraction reactions do not result in chain branching since the ·OH becomes $H_2O$, whereas ·O becomes ·OH

## (a) Reactions with Paraffins

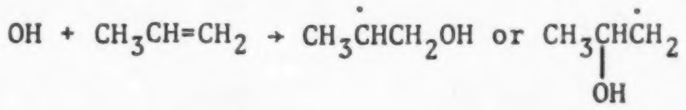
The paraffin-OH reaction results in hydrogen abstraction, an alkyl radical and water being formed.

$$RH + OH \rightarrow R\cdot + H_2O$$

Note that this is a chain transfer rather than a chain branching reaction. The rate of reaction of an individual hydrocarbon with OH generally increases with the number of H atoms on the molecule, especially secondary and tertiary hydrogens. Rate constants for these reactions are compiled in Johnston et al. (1970).

## (b) Reaction with Olefins

Hydroxyl radicals react with olefins by addition at the double bond. Morris et al. (1971) have observed OH adducts directly in the reactions of OH with $C_2H_4$ and $C_3H_6$.

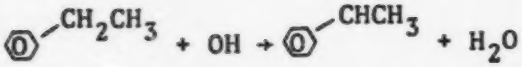


$$OH + CH_3CH{=}CH_2 \rightarrow CH_3\dot{C}HCH_2OH \text{ or } CH_3\underset{\underset{OH}{|}}{CH}\dot{C}H_2$$

Recently, the rate constants for OH attack on several olefins have been measured by Morris and Niki (1971). Their results indicate that, for a given olefin, the rate constant for the OH-olefin reaction is about ten times greater than for the corresponding O-olefin reaction. Less is known about the reactions of the OH adduct radical that take place subsequent to the initial addition, although possible reaction mechanisms have been proposed by Westberg and Cohen (1969), Niki et al. (1972) and Hecht and Seinfeld (1972). As such, it is important to establish the reactivity of this adduct with respect to NO oxidation and to identify its decomposition products. With this information the role of the OH-olefin reaction in smog formation can be firmly established.

(c) Reactions with Aromatics

It is current speculation that hydroxyl radicals abstract alpha hydrogen atoms from branched aromatics in the same manner as we have assumed occurs in the case of O.



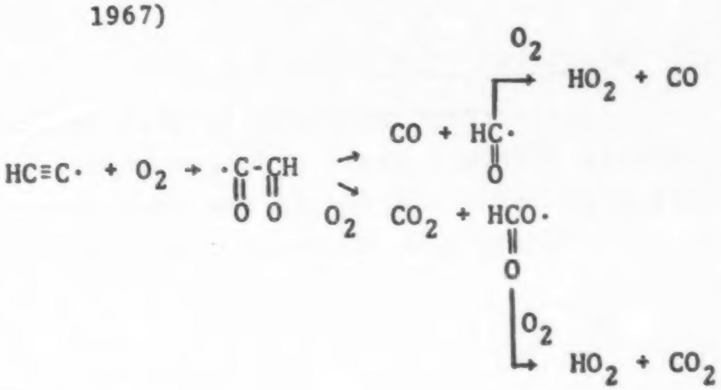
If the reaction does, indeed, proceed as indicated, it would once again be a chain transfer rather than a branching step. The arguments presented earlier concerning the delocalization stabilization of free radicals formed by H abstraction from alkyl and dialkyl aromatics also hold in this case. It is also possible that OH adds to the ring. At this time, however, the experimental evidence is insufficient to permit specification of the exact mechanism of the reaction.

(d) Reactions with Acetylene

The OH radical is generally thought to react with acetylene by abstracting a hydrogen atom.

$$OH + HC{\equiv}CH \rightarrow HC{\equiv}C\cdot + H_2O$$

The acetyl radical thus formed may react in air as follows (Stevenson and Tipper, 1967)



The overall result of the indicated reaction sequence, then, is a chain transfer, with $HO_2$ replacing OH as the active species. Semi-quantitative measurements of the OH-acetylene reaction reported in Johnston et al. (1970) indicate that at ambient temperatures the reaction is quite slow, being about as fast as the OH-ethane reaction. We recommend that a quantitative value of OH-acetylene rate constant be obtained. If, indeed, it is a slow reaction, then the photochemical oxidation of acetylene will not contribute appreciably to smog formation.

### (3) $O_3$ Oxidation Reactions

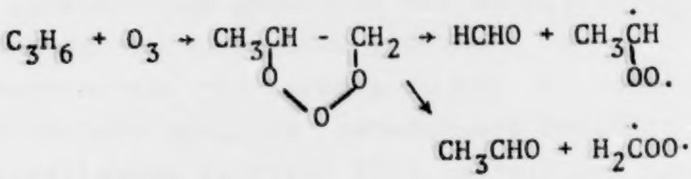
Ozone begins to form in significant amounts when the $NO_2$ concentration reaches a level about twenty five times that of the NO concentration. Ozone is not nearly as strong an oxidizing agent as O or OH. However, concentrations of ozone of about .25 ppm or greater are not uncommon in polluted atmospheres; at these concentrations ozone and olefins will react at appreciable rates

#### (a) Reactions with Paraffins and Aromatics

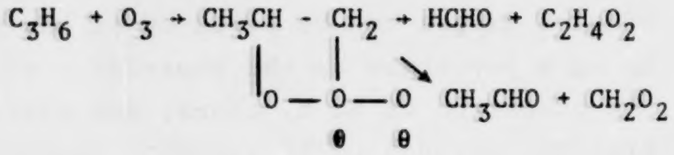
Ozone does not react at a significant rate with either paraffins or aromatics. Several paraffin-ozone rate constants have been determined, and these have been summarized by Peters and Wingard (1970).

(b) Reactions with Olefins

The reactions of ozone with olefins in the gas phase have been studied extensively during the past two decades, and rate constants for the ozonolysis reaction are available for a large number of olefins (see Johnston et al., 1970 ). However, the mechanism of olefin-ozone reaction in the gas phase has not yet been established, and the initial decomposition products have not yet been conclusively identified. Although the exact mechanism is still unresolved, ozone is thought to add to the olefin double bond in the liquid phase to form a molozonide intermediate, the molozonide then decomposing into an aldehyde and a diradical (or "zwitterion").



Ozonolysis in the gas phase may proceed by this same mechanism or by allylic oxidation, which would lead to the same decomposition products.



$$C_3H_6 + O_3 \rightarrow \underset{O-\overset{}{\underset{\oplus}{O}}-\underset{\ominus}{O}}{CH_3CH - CH_2} \rightarrow HCHO + C_2H_4O_2$$

$$\searrow CH_3CHO + CH_2O_2$$

We recommend that the mechanism of the reaction in the gas phase be firmly established. In particular, it will be important to identify the transient intermediates such as diradicals, and to establish subsequent reactions of these species in polluted air.

### (c) Reactions with Acetylenes

Rate constants for reactions of ozone with acetylene and higher alkynes have been determined by DeMore (1971). The low values for the rate constants indicate that these reactions have little, if any, influence on the smog formation process. (Typically the rate constants for ozonolysis of acetylenes are about $10^{-4}$ $ppm^{-1}min^{-1}$.)

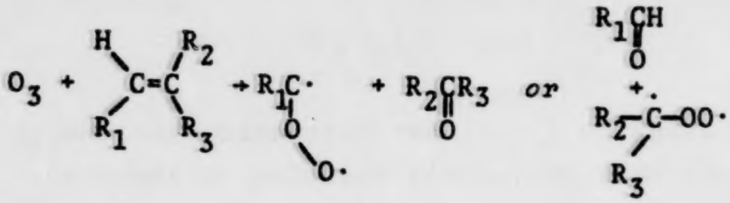
### (4) Singlet Oxygen

There have been numerous recent publications concerning the possible role of singlet molecular oxygen in smog formation. (For a review see Pitts et al., 1969 and Johnston et al., 1970.)

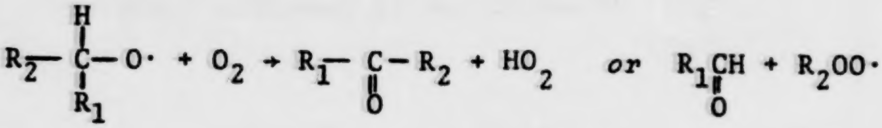
Singlet oxygen can be produced in the air by such processes as the photolysis of ozone, the oxidation of NO by ozone, and energy transfer through collision with excited molecules. The concentration of singlet oxygen has not been determined in the atmosphere, but Frankiewicz and Berry (1972) have estimated that it is only about two orders of magnitude greater than that of O. In view of those low concentrations and the low rate constants for $^1O_2$ - olefin reactions summarized by Herron and Huie (1970) we may assume that singlet oxygen is probably not a major hydrocarbon oxidant.

### b. The Mechanisms of Oxidation of Oxygenated Hydrocarbons

Seizinger and Dimitriades (1972) have shown that aldehydes and ketones are present in the exhaust of automobile engines fueled by simple hydrocarbons. As indicated earlier, oxygenates constitute only about 1.5% of the hydrocarbons found in auto exhaust. Thus, the most important source of atmospheric oxygenates may be the oxidation of hydrocarbons and the decomposition of free radicals. Of the oxygenates produced in this manner, aldehydes seem to form more readily than ketones, for ketones are produced only when reaction occurs at a carbon atom bonded to at least two other carbons atoms in the molecule being oxidized, e.g.



or



$$R_2-\underset{R_1}{\overset{H}{C}}-O\cdot + O_2 \rightarrow R_1-\underset{O}{\overset{}{C}}-R_2 + HO_2 \quad or \quad R_1\underset{O}{CH} + R_2OO\cdot$$

etc.

Leighton (1961) has supported this view, concluding that the atmospheric processes that result in the formation of aldehydes apparently do not generate ketones in comparable amounts. In this section, therefore, we focus our attention on the reactions of aldehydes.

Aldehydes will photodissociate in sunlight and react with O atoms, forming alkyl radicals (and, thus, peroxyalkyl radicals), formyl radicals (and, thus, hydroperoxy radicals), and hydroxyl radicals. Therefore, the reactions of aldehydes can contribute significantly to the initial accumulation of $RO_2$, $HO_2$, and OH.

(1) Photolysis

Aldehydes photodissociate in sunlight at wavelengths greater than 3000 Å in chain initiating reactions.

$$RCHO + h\nu \rightarrow R\cdot + \cdot CHO$$

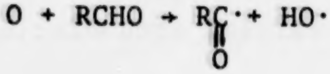
Leighton (1961) has estimated that the rate of this photolysis reaction is about one-hundredth the rate of $NO_2$ photodissociation. In the case of formaldehyde, a second primary photodissociation is possible (Calvert et al., 1972).

$$HCHO + h\nu \rightarrow H_2 + CO$$

This reaction pathway, which does not directly result in the formation of free radicals, has a probability of occurrence about equal to that for the chain initiating reaction.

### (2) O Atom Oxidation Reactions

The typical rate constant for the O-aldehyde reaction falls between those of the O-olefin and O-paraffin reactions. The reaction is one of chain branching

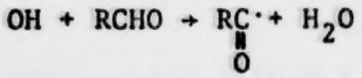


$$O + RCHO \rightarrow R\underset{\underset{O}{\|}}{C}\cdot + HO\cdot$$

resulting in the formation of an acyl radical.

### (3) OH Oxidation Reactions

Hydroxyl radicals abstract a hydrogen atom from aldehydes forming an acyl radical and water.



$$\mathrm{OH} + \mathrm{RCHO} \rightarrow \mathrm{R}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot + \mathrm{H_2O}$$

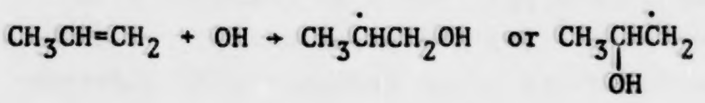
The chain transfer reaction takes place about as rapidly as the reaction of OH with propylene. The rate constants for the reaction of OH with formaldehyde and acetaldehyde have been determined by Morris and Niki (1971). They are both about 22,500 $ppm^{-1}min^{-1}$ as compared with 25,000 $ppm^{-1}min^{-1}$ for the propylene-OH reaction. Thus, the reactions of OH radicals with aldehydes may serve as an important mechanism for removal of aldehydes from the atmosphere and as a significant source of free radicals capable of oxidizing NO.

### (4) $O_3$ Oxidation Reactions

The kinetics of the ozone-aldehyde reactions apparently have not been studied in detail. Leighton (1961) has estimated that the reaction is probably slower than the ozone-olefin reaction by about two orders of magnitude. As a result, this reaction probably does not contribute significantly to the overall smog formation process. However, organic acids, constituents of atmospheric aerosols, might form as a result of the ozonolysis of aldehydes. Consequently, it would be worthwhile to determine the rate constant, mechanism, and products of the ozonolysis reaction for several different aldehydes.

### c. Free Radical Reactions

The reaction between a single hydrocarbon species and a particular oxidant (say, O, OH, or ozone) often yields more than one set of products. For instance, in the case of the OH-propylene reaction, OH can add to either side of the double bond.



$$CH_3CH{=}CH_2 + OH \rightarrow CH_3\dot{C}HCH_2OH \quad \text{or} \quad CH_3\underset{OH}{\underset{|}{C}}H\dot{C}H_2$$

Adding to the difficulty of identifying or specifying the products of initial reaction steps involving free radicals is the fact that the fate of the radicals in subsequent reactions is often unknown. For example, it has not yet been determined if the products of the propylene-OH reaction are stable entities or if they decompose rapidly as a result of the excess heat supplied by the formation reaction. Because of uncertainties such as this, it is extremely difficult to estimate the overall chain length and number of NO molecules oxidized per OH-propylene reaction. Difficulties in specifying products and estimating chain lengths are, of course, enhanced as the complexity and size of the hydrocarbon species involved in the reaction increases.

In considering the reactions of highly substituted molecules, the number of NO molecules oxidized per hydrocarbon molecule consumed will depend strongly upon the degree of fragmentation (i.e.

the degree of branching) taking place, as well as upon the rate of the initial hydrocarbon oxidation reaction. In particular, high molecular weight hydrocarbons are often considerably more reactive with respect to NO oxidation than are smaller, straight-chain hydrocarbons. For a classification of NO oxidation rates by hydrocarbon type the reader is referred to the summary in Johnston et al. (1970).

As noted in Chapter II, the oxidation of the various classes of hydrocarbons by O, OH, and ozone results in the formation of several different types of free radical products. Some of these radicals, notably alkyl and acyl, are extremely reactive, combining immediately with molecular oxygen to form peroxyradicals.[*] In this discussion we give our attention only to the more slowly reacting radicals,

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If the alkyl radical is a product of highly exothermic reaction, it is possible that the $O_2$ might abstract a hydrogen at a position alpha to the free radical, forming an olefin rather than adding at the site, e.g.

$$CH_3CH_2\dot{C}HCH_3 + O_2 \rightarrow CH_3CH_2CH{=}CH_2 + HO_2 \quad \text{or}$$
$$CH_3CH{=}CHCH_3 + HO_2$$

This reaction is observed in high temperature flames (i.e. 425°C) (Benson, 1968). At ambient temperatures, however, probably no more than 1% of the $R\cdot{-}O_2$ reactions proceed in the manner, the remaining 99% resulting in the formation of the conventional peroxyalkyl radicals. Even so, this type of reaction may be a source of olefins in the oxidation of paraffinic systems and, as a consequence, merits further experimental investigation.

| | |
|---|---|
| $RO_2$ | alkylperoxy |
| $RCO_3$ | acylperoxy |
| RO | alkoxy |

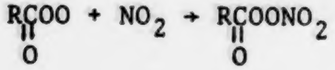
those that substantively influence the photochemical reaction process. We note that the $HO_2$ radical, closely related to $RO_2$, has been discussed earlier, in the section dealing with inorganic reactions.

Peroxyradicals enter into reactions of interest with three species: NO, $NO_2$, and ROO. Unfortunately, the rate constants for each class of reactions is presently unknown. The primary mechanism by which NO is thought to be oxidized to $NO_2$ without the consumption of ozone is through reaction with peroxy radicals.

$$RO_2 + NO \rightarrow NO_2 + RO$$

The rate of this type of reaction probably decreases as the size of the R group increases, because large R groups have a greater number of vibrational degrees of freedom over which to distribute the energy of the free radical. Demerjian et al. (1973) have estimated that the rate constants for the $CH_3O_2\cdot$-NO and $CH_3\underset{\underset{O}{\|}}{C}O_2\cdot$-NO reactions are 910 and 470 $ppm^{-1}min^{-1}$ respectively. Spicer et al. (1971), however, have found the $CH_3O_2$-NO reaction to be quite slow. As the time to the $NO_2$ peak predicted by kinetic mechanisms currently in use is quite sensitive to the magnitude of this rate constant, it is of interest to establish its value for the reaction of NO with each of several different peroxy radicals.

As NO is oxidized and $NO_2$ accumulates during smog formation, the reaction of peroxy radicals with $NO_2$ becomes increasingly important. If the peroxy radical is an acyl peroxy radical, stable products, peroxyacylnitrates (PAN), will form.



$$R\underset{\overset{\|}{O}}{C}OO + NO_2 \rightarrow R\underset{\overset{\|}{O}}{C}OONO_2$$

Formylperoxynitrates, however, are thought to be extremely unstable, if, indeed, they do form at all; they have never been observed in smog chamber studies. Similarly, alkylperoxynitrates and arylperoxynitrates have yet to be observed in smog chambers, and it is not known whether or not these species are stable. Rather, the reaction of peroxyalkyl-radicals with $NO_2$ might go through a peroxynitrate transition state, resulting in the formation of $NO_3$.

$$ROO + NO_2 \rightarrow [ROONO_2] \rightarrow RO + NO_3$$

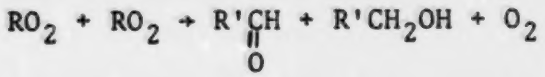
This reaction is, however, endothermic and thus has a low probability of occurrence.

Given these gaps in knowledge, it is clearly of interest to determine the mechanism of the $RO_2$-$NO_2$ reactions and to estimate the associated rate constants. This information will be particularly useful in the validation of kinetic mechanisms, as the magnitudes of the reaction parameters strongly affect the predicted asymptotic level of ozone, the height of the $NO_2$ peak, and the rate of decay of $NO_2$ after the peak.

The population of peroxy radicals in the smog system is limited by radical-radical recombination reactions. These reactions may be direct recombinations to form a peroxide and $O_2$

$$RO_2 + RO_2 \rightarrow ROOR + O_2$$

or disproportionations to form an aldehyde (or ketone), an alcohol, and $O_2$.



$$RO_2 + RO_2 \rightarrow R'\underset{\overset{\|}{O}}{C}H + R'CH_2OH + O_2$$

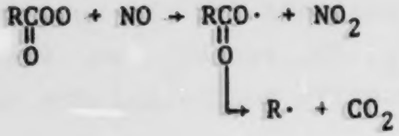
Because the rate of radical-radical recombination influences the radical population and the time scale of NO oxidation, the rate constants for this class of reactions must also be determined.

It had been thought that, because of the high rates of the OH-olefin reaction, peroxyradicals might also react rapidly with hydrocarbons. However, Hendry (1973) recently studied the reaction of $HO_2$ with olefins and of $CH_3O_2$ with tetramethylethylene and butadiene in the liquid phase and reached a different conclusion. He found that the rate constants for the reactions are quite small, on the order of $10^{-4} ppm^{-1} min^{-1}$. It is likely that this reaction is also slow in the gas phase and can be ignored in accounting for the consumption of hydrocarbons.

Alkoxy radicals are formed as a product of the $RO_2$-NO reaction and some $RO_2$-$NO_2$ reactions

$$RO_2 + NO \rightarrow RO + NO_2$$

(Peroxyacyl radicals react with NO to form acylate radicals and $NO_2$; the acylate radical, however, is very unstable and loses $CO_2$, forming an alkyl radical.)



$$R\underset{\underset{\displaystyle O}{\|}}{C}OO + NO \rightarrow R\underset{\underset{\displaystyle O}{\|}}{C}O\cdot + NO_2$$
$$\hookrightarrow R\cdot + CO_2$$

Alkoxy radicals react predominantly with $O_2$ to form an aldehyde and $HO_2$;

$$RO + O_2 \rightarrow RCHO + HO_2$$

the rate constant for the pseudo-first order reaction has been determined by Heicklen (1968) to be about $4.4 \times 10^3\ ppm^{-1}min^{-1}$, when R is $CH_3$ or $C_2H_5$. The only competing reactions might be those of RO with NO and $NO_2$ to form nitrites and nitrates,

$$RO + NO \rightarrow RONO$$

$$RO + NO_2 \rightarrow RONO_2\ .$$

However, the low concentrations of nitrites and nitrates observed in smog chamber product analyses suggest that these reactions are not sufficiently rapid to be important.

We recommend that an effort be made to establish the mechanism and determine the rate constants for the reactions of several organic peroxy radicals with NO, $NO_2$, and $RO_2$. Also of interest, but of lesser importance at this time, is the study of rate constants for the reactions of oxy radicals with $O_2$, NO, and $NO_2$, and the investigation of alternative mechanisms for the $R\cdot - O_2$ reactions.

### d. Summary

In this section we have examined the reactions of paraffins, olefins, aromatics, acetylenes, and aldehydes with the most important oxidants found in the atmosphere. We have also discussed the possible subsequent reactions of the free radical products of these oxidation reactions. During the course of the discussion we have identified a number of reactions that require investigation. In summarizing our findings, we recommend that the following studies merit immediate attention.

(1) Branched aromatics constitute approximately 20% of the hydrocarbon mix in polluted atmospheres such as that of Los Angeles.

Thus, the rate of reaction of branched aromatics with both O and OH should be measured. The products of these oxidation reactions should also be determined.

(2) The rate of oxidation of NO predicted by kinetic mechanisms depends strongly upon the products assumed to form in the OH-olefin reactions. Thus, subsequent decomposition reactions of the OH-olefin adducts should be identified.

(3) Although the $O_3$-olefin reaction does not appear to consume a significant portion of the total olefin, the suggested intermediates of the reaction, so-called zwitterions, may be powerful oxidants. Thus, the mechanism and products of the $O_3$-olefin reaction require further study. It is also of interest to investigate the reactions of zwitterions with atmospheric pollutants.

(4) Peroxy radicals are thought to be important oxidizers of NO. It is believed that they also react with $NO_2$ to form stable products. The importance of these processes cannot be fully assessed, however, until the rate constants for these reactions have been determined.

(5) The population of free radicals in photochemical smog may possibly be limited by the rates of radical-radical recombinations. Thus, the rates of these termination reactions should be measured.

## B. Investigation of Particle Growth Processes and the Effect of Particles on Smog Formation Kinetics

It has long been recognized that atmospheric photo-oxidation processes are frequently accompanied by aerosol* formation. Despite this early recognition, the available smog chamber data and the existing atmospheric data have been neither sufficient nor adequate to characterize fully either the physical or chemical mechanisms which govern photochemical aerosol formation in the atmosphere or the interaction of aerosols with the homogeneous gas-phase formation of photochemical smog. This deficiency in understanding is due to the experimental difficulties associated with (1) measuring the distributional properties of aerosols and (2) generating a representative aerosol distribution.

Ultimately, it will be useful to formulate a model for the combined gaseous and particulate components of an urban atmosphere. The success of such an endeavor depends upon our degree of understanding of aerosol

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* suspended liquid droplets and solid particles

(1) sources
(2) growth kinetics, and
(3) interactions with the gas phase constituents.

The first of these topics must necessarily be investigated primarily in the atmosphere; discussion of it is thus deferred until Chapter VI. The second and third topics, however, can be investigated meaningfully in the laboratory and will be discussed here.

### 1. Particle Formation and Growth

Aerosols can be classified into two distinct groupings--the larger, so-called "primary" aerosols which consist of particulates *introduced* into the atmosphere from sources (e.g. dust, smoke) and the smaller, sub-micron size, "secondary" aerosols which are *produced* in the atmosphere by condensation and chemical reaction. We consider the secondary aerosols here specifically because they are

(1) responsible for the reduction in visibility associcated with smog
(2) implicated in aggravating respiratory ailments, and
(3) products of photochemical smog.

Both chemical and physical mechanisms play important roles in aerosol formation and growth. Chemical reactions provide species convertible from the gas to the particulate (liquid or solid) phase and may take place in the particles themselves. Physical processes such as nucleation, condensation, absorption, adsorption and coagulation are primarily responsible for determining physical properties; i.e., number concentration, size distribution, optical properties, settling properties, etc. of the formed aerosols. Based on the results of the 1969 Pasadena Smog Experiment (Chapter VI), Husar and Whitby (1973) have proposed the following mechanism for photochemical aerosol formation: "The driving force for the gas-particle conversion is provided by a gaseous photochemical reaction or chain of reactions. The gaseous reaction(s) produces a supply of molecular species (or radicals) which, upon collision with each other, agglomerate and form molecular clusters; i.e., homogeneously nucleate. If suitable aerosol particles or ions are present, the monomers or radicals deposit preferentially on the existing surfaces and thus the nucleation is heterogeneous. The growth rate of the newly formed particles is controlled by the diffusion rate, i.e., the collision rate of the condensable species. The condensation* itself may be physical (governed by supersaturation) or chemical (if the condensable species react with each other upon collision). If the concentration of the droplets is sufficiently high, they may interact by coagulation."

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* In this context, the term "condensation" is used to designate a diffusion controlled growth process, regardless of the nature of the accommodation process; i.e., physical or chemical.

In an initially particle-free chamber, Husar and Whitby found that the chronological evolution of a photochemical aerosol may be characterized by:

1. Initial rapid increase in total number concentration by nucleation.
2. Coagulation when the aerosol concentration reaches a sufficiently high level (maximum concentration when production rate equals coagulation rate).
3. The attainment of a steady-state surface area sufficient to accommodate all the vapor (the nucleation rate then diminishes). Decay of number concentration by coagulation. Gas-particle conversion rate associated with the steady-state surface areas.

Although particle-free systems have been the subject of most smog chamber studies, it is well-recognized that the study of the growth of atmospheric aerosols must include consideration of the presence of foreign nuclei and therefore of heterogeneous nucleation. Heterogeneous nucleation is extremely complex, depending on the size distribution and surface properties of the foreign nuclei, as well as on the concentration and chemical composition of the vapor. There is considerable evidence that in Los Angeles the mode of nucleation of photochemical aerosols is primarily heterogeneous. Thus, the total nuclei count is governed by ground sources and not by self-nucleation (Husar and Whitby, 1973).

In order to investigate the physical and chemical behavior constituents of photochemical smog in the formation and growth mechanisms of aerosols, we recommend that the following studies be undertaken:

(1) A complete chemical identification of the *individual* constituents of secondary aerosols should be made. Combined gas chromatography-mass spectrometry systems offer promise in this regard. Organic species represent a significant portion of the atmospheric photochemical aerosol on a weight basis (Friedlander, 1973). Only after the relative abundance of individual species (e.g. organic acids and diacids, aldehydes, paraffins, polynuclear aromatics, organic and inorganic nitrates, sulfates, $H_2O$, etc.) in the aerosol is assessed will it be possible to postulate a chemical mechanism for the growth of particles. With such information, however, it will also be possible to assess the importance of aerosols as a sink for gas-phase pollutants.

(2) The threshold levels of specific hydrocarbons and $SO_2$ should be established for a polluted atomosphere in which aerosol is formed. Hydrocarbons selected for investigation should be those which participate in reactions leading to the formation of oxidation products observed in the atmospheric aerosol (Task 1). For

instance, if adipic acid ($C_6$ diacid) were observed during the first task, it would be necessary to determine threshold levels of cyclohexene and 1,7-octadiene necessary for the formation of aerosol. Further, threshold levels of hydrocarbon mixtures must be established. In so doing, it will be possible to judge the importance of preferentially contolling the emissions of individual hydrocarbons in an effort to meet a given visibility standard.

(3) The rate of chemical oxidation of $SO_2$ and $NO_2$ at the surfaces of aerosols should be determined. Although sulfates in particles can result from the photochemical oxidation of $SO_2$ in the gas phase, followed by condensation, it is also possible that (1) $SO_2$ is oxidized in liquid droplets through reaction with $O_3$ or metal ions or (2) $SO_2$ is catalytically oxidized on the surfaces of solid particles. Similarly, nitrate formation results from the reaction of $NO_2$ with NaCl, a pathway for nitrate production additional to that provided by the gas phase $NO_3$ reaction.

(4) The effects of changes in factors such as temperature, humidity, stirring intensity, and turbulence level, all of which are known to affect the growth rates and size distributions of particles, must be quantitatively assessed.

## 2. The Effect of Particles on Smog Formation Kinetics

We have thus far examined the ways in which photochemical smog can contribute to aerosol formation and growth. Because of the high surface area that aerosols present to the gas phase, it is also possible that their presence affects the *rate* of formation of smog. Before meaningful studies can be carried out, however, we must be able to reconstruct experimentally the measured atmospheric spectrum of aerosol properties, notably with respect to size and chemical composition. If this effort is successful, it will then be possible to determine if the kinetics of the overall formation process of smog is affected by the presence of particles. For example, particles may quench free radical chains or adsorb free radical initiators such as $NO_2$ or $HNO_2$, thereby slowing the oxidation of NO, or they may oxidize NO at the surfaces if they are catalytically active or if they contain strong oxidants, thereby accelerating smog formation. If aerosols are shown to affect the rate of smog formation, it would then be useful to alter the characteristics of the simulated aerosol in the chamber to investigate the effects of changes in (1) chemical composition and (2) number and size distribution on the resultant smog kinetics. Only upon completion of such studies can validation of kinetic mechanisms be meaningfully undertaken using data collected in smog chambers in which particles were present initially.

## V. CONTROLLED EXPERIMENTAL STUDIES IN SMOG CHAMBERS

The formation of photochemical smog occurs in an extremely complicated system, one in which meteorology, continuous emissions of pollutants, and photochemistry all play important roles. In order to isolate the effects of photochemistry from other variables present in an atmospheric environment, investigators have simulated the chemical reaction process by irradiating the primary pollutants in static reactors, so-called smog chambers, some of the results of which are described briefly in this chapter. The observed results must be interpreted with great care, however, for even in a smog chamber factors other than the photochemistry can still influence the course of the overall smog formation process. We therefore devote much of this chapter to procedural considerations such as wall effects, radiation simulation, analytical procedures, and reproducibility of experiments. In short, we point out the necessity of completely characterizing the smog chamber before experimental studies are conducted. Finally, we discuss ways in which an operating system can be used to generate data for the validation of kinetic mechanisms, to demonstrate interactions between specific pollutants and typical urban air pollution samples, and to investigate scavenging processes that occur in the natural environment.

### A. Chamber Effects

A very important question to examine at the outset of experimental smog chamber studies is *how and to what* *degree the design, construction, and operation of the chamber affect the observed results.* Similar smog chamber experiments performed in different chambers, but with the same hydrocarbons, have not all exhibited the same concentration-time behavior. Because initial concentrations are similar, it appears that effects characteristic of the chambers themselves are influencing the courses of the experiments. Possible explanations for the disparate behavior include differing degrees of mixedness, surface effects, and irradiation intensity between chambers. Indeed, experiments performed in a single chamber are not always reproducible in the same chamber a month later (Westberg, 1972). The problem of non-reproducibility is quite possibly serious enough to render much of the existing smog chamber data unsuitable for the purposes of model validation. If smog chamber experiments are to be used as a tool for broadening our understanding of smog formation, individual chamber effects must be minimized or eliminated. At the very least they must be understood quantitatively. In this section, therefore, we undertake to point out what we consider to be the most critical of chamber effects. So that the examination of chamber effects can be comprehended in the perspective of current experimental methods, however, we begin our discussion by surveying the various types of smog chambers in common use.

Smog chambers can be classified into three general categories. The earliest and most popular were the large environmental chambers having volumes from fifty to five hundred cubic feet. The large volume is appealing because of the "wall-less" nature of the atmosphere being simulated.

Due to their size, these chambers have traditionally been constructed of the most convenient materials, e.g. plate glass, aluminum, or Teflon-lined materials. Although the size has as an advantage reduced surface to volume ratios, there are several inherent shortcomings in this type of chamber:

1. Due to the large surface areas involved, cleaning of surfaces can be a long and tedious task, one which is often neglected.
2. Direct measurement of light intensity in these chambers by the conventional procedure (see part 3 of this section) requires that all of the $O_2$ in the chamber be displaced by an inert gas such as nitrogen. This is both difficult and expensive. (Alternately, $k_1$, the photolysis rate of $NO_2$, can be determined in a smaller bag inside the chamber, but this procedure requires proper and accurate compensation for the absorption of light by the bag.)
3. Unless the chamber is carefully designed and stirred, a significant percentage of the chamber contents may not be well-mixed.
4. A large bank of analytical instruments must be available to monitor the chemistry, and each of these instruments must be recalibrated regularly to insure its accuracy. (A notable exception to the former problem is use of long path infrared systems (to be discussed shortly),

in that the single spectrometer is capable of monitoring all of the major contaminants.)

A second type of smog chamber is simply a plastic or Teflon bag. The chief advantage of bags is that constant pressure is maintained during sampling without the necessity of dilution due to collapse of the enclosing surface. Because of their reduced volume, bags are convenient to work with and have the advantage of allowing easier measurement of the light intensity. Bags, however, suffer the disadvantages cited above, as well as having

1. a high surface to volume ratio
2. no facilities for mechanical stirring, and
3. pollutant absorption on, or reaction with, the surface material.

The third popular type of smog chamber is the long path infrared spectrometer (LPIR) with a small (∿100 liters) reactor enclosing the optics. LPIR's have as an advantage the fact that all the pollutants are monitored using a single instrument, the spectrometer, so that only the optics require adjustment to assure accurate monitoring. The reactors, however, have less favorable surface to volume ratios than do environmental chambers, and they are very difficult to clean by wet methods. Removal of the reactor for cleaning is a delicate and time consuming task, and care must be taken not to misalign the optics. Finally, mechanical stirring devices cannot be introduced into such a system.

In the past considerable effort has been expended in simply identifying the precursors of atmospheric reaction products and in obtaining general information about the importance of such factors as the influence of hydrocarbon to $NO_x$ ratios on the level of oxidant formed. Each of the three systems described above can be used in performing this task. However, the general aspects of smog formation are now understood reasonably well. Thus, future scientific inquiry must necessarily be conducted in a detailed, quantitative manner, if it is to be justified. This means that, beyond monitoring the concentration-time behavior accurately in new smog chamber runs, the effect of each operating parameter of the system on the overall smog process must be carefully assessed. Until this is the case, it will not be possible to establish a correspondence between smog chamber experiments carried out under identical initial conditions, but performed in different chambers. In short, it will not be possible to distinguish between the two categories of factors contributing to the observed (apparent) photochemistry:

1. those associated with the gas phase chemistry (Chapter IV) and
2. those associated with the interactions of the operating chamber with the chemistry.

It is for this reason that we begin our discussion of controlled experimental studies in smog chambers by considering effects associated with the experimental system which can alter the course of the reaction and thus reduce accuracy and quality of the reported data.

In our estimation, those factors causing similar smog simulation experiments to differ from chamber to chamber (and, for that matter, from chamber to atmosphere) fall into three broad classes:

(1) degree of stirring and mixedness in the chamber

(2) surface effects, and

(3) radiation simulation.

The first of these, the effect of gas-phase heterogeneities on the rate of the overall photochemical reactions, has been discussed extensively in Chapter III. It is a problem that, once recognized, can be solved by careful chamber design. The key point is that *the experimenter must insure that the contents of his chamber are well-mixed so that the chamber is in practice an ideally-mixed vessel.* Only then can the concentration changes be represented by the usual ordinary differential reaction rate equations.

The complete elimination of surface effects is probably an impossible goal. Rather, we must be satisfied with controlling and, at the very least, understanding the influence of the surfaces on the photochemistry. The extent of surface-gas phase interactions can be determined by measuring the rates at which known concentrations of pollutants adsorb or decompose on the walls, and those values should complement the gas phase material balance to account for the entire initial reactant charge (less that lost by sampling and dilution).

The problems associated with radiation simulation are two-fold: (1) the achievement of a uniform light intensity distribution throughout the chamber and (2) the careful measurement of light intensity. Solution to the former problem can be achieved by careful placement of the lamps. Light intensity measurement techniques are presently available; however, they are cumbersome, particularly those which require the complete displacement of $O_2$ from the reactor. Convenient methods must be developed to encourage the routine monitoring of light intensity. These three factors, then, represent the most serious influences of smog chambers on the homogeneous gas phase chemistry. Given a quantitative assessment of each of these operating parameters, however, it will become possible to extract meaningful kinetic data from smog chamber experiments.

### 1. Stirring and Mixedness in the Chamber

Although smog chambers are often thought of as atmospheric or environmental simulation chambers, one of their primary functions is to permit the study of the macroscopic smog kinetics in an uncomplicated and controlled system. Variables that the experimenter may wish to control are the concentrations of the reactants, the temperature and humidity of the chamber, and the radiation intensity. Another variable of interest, one that is more difficult to define precisely, is the degree of mixing in the chamber. We have already seen in Chapter III that heterogeneities in the reactant-gas mixture will lead to the observation of "apparent" kinetics, that is reaction rates that differ from those occurring in a well-mixed, homogeneous system. Certainly, the atmosphere is not a homogeneous reactor; however, if smog chambers are to be used as a tool for studying chemistry solely, they must, ideally, be well-mixed. The achievement of a homogeneous system is primarily a matter of careful design.

The flow patterns observed in a smog chamber depend critically on two factors, the geometry of the chamber and the stirring apparatus employed. In some conventional smog chambers equipped with mixing devices, it has been estimated that a poorly mixed region characterized by laminar (versus turbulent) flow develops at the walls or boundary of the chambers and can encompass upwards of 25% of the total volume of the chamber (Liu, 1972). The judicious placement of mechanical stirrers can reduce that problem substantially.

## 2. Surface Effects

Ideally, the presence of surfaces in the reactor should not affect the results of a smog chamber experiment. In practice, however, there is little reason to believe that is the case. Carbon and nitrogen material balances for the gas phase materials over the course of an irradiation have often been poor. For example, Altshuller et al. (1970) reported that they were able to account for only 3% of the initial carbon and 10-20% of the initial nitrogen after a

6 hour irradiation of toluene in $NO_x$. Part of the difficulty may be explained by the failure of many investigators to measure all of the products of the photochemical reactions. In the irradiation of ethylene-$NO_x$ mixtures, CO and $CO_2$ are important carbon-containing products which are not always monitored (Gay and Bufalini, 1971). The irradiation of aromatic-$NO_x$ mixtures results in the formation of acetylene as a major carbon-containing product; failure to measure that species probably accounts for the poor carbon balance reported by Altshuller et al. (1970) for toluene and m-xylene. Another reason for poor carbon balances is that free radicals and polar species such as aldehydes and organic acids are adsorbed on the walls. The relative contributions of these two effects in accounting for the initial carbon charge has yet to be assessed in quantitative terms.*

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* Other possible reasons for poor material balances are (1) that strongly polar products such as organic acids may be lost to the sides of sampling tubes leading to the monitoring instrument and (2) that the analytical instruments may be improperly calibrated.

The major reason for poor nitrogen balances is definitely attributable to surface effects.* The work of Gay and Bufalini (1971) supports this hypothesis, in that they were able to obtain a consistent nitrogen balance when they included the nitrate and nitrite washed from the walls of their irradiation vessel. Their results suggest that the presence of surfaces affects both the observed rates and the product distributions.

The necessity of achieving and maintaining a mass balance for carbon and nitrogen over the entire course of a photochemical smog experiment cannot be overemphasized. Without a mass balance there is no assurance that all the important products in the system are being detected. Nor can one be sure that the products have been measured accurately. Certainly, the problems associated with achieving a consistent material balance are great, but a 100% balance should be the goal.

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* It had been thought that molecular nitrogen might be a product of the ethylene-$NO_x$ reactant system (Bufalini and Purcell, 1965), but Gay and Bufalini (1971) have since disproved this hypothesis.

While it seems unlikely that surface effects can ever be completely eliminated, it is possible to identify, quantify, and minimize the various types of surface-gas interactions. Topics to be discussed in this section include studies of the rates at which various chamber surface materials adsorb constituents of smog, the effect of surface to volume ratios on the rate of wall adsorption, the cleaning and preparation of the surfaces, and the effects of wall temperature and the amount of water adsorbed on the walls on the rates of wall reactions.

### a. Surface Materials and Wall Adsorption Studies

Recently, several groups have begun to explore the influence of various surface materials on the loss rate of pollutants in chambers. At Lockheed Missiles and Space Company, Jaffee (1972) is investigating the effect of four surface materials on the results observed in his chamber during hydrocarbon-$NO_x$ irradiations. They include Pyrex, stainless steel, aluminum, and Teflon. In work recently completed, Sabersky et al. (1973) have determined the loss rate of ozone in a small chamber containing large sheets of several different materials. They found that the decomposition rate of ozone was the least for aluminum and plate glass, was 6 times greater for Lucite, 24 times greater for polyethylene, and almost 100 times greater for neoprene. In their experiments the temperature of the system was maintained at 72°F ±1°F and the relative humidity at 50% ±5%. Mixing was accomplished through the use of several large fans. These investigators are presently carrying out a similar set of experiments using nitric oxide.

Tentative results for the effects of Teflon on reaction dynamics are available from two sources. Holmes (1973) of the California Air Resources Board has postulated that ozone is absorbed by the Teflon surface of the ARB chamber during cleaning operations, at which time the walls are exposed to 20 to 40 ppm of ozone for 24 hours. His conjecture is based upon the fact that ozone continues to appear in his nitrogen-filled chamber for several days after the original ozone has been flushed from the system, the ozone presumably being re-emitted by the Teflon. It is important to investigate this phenomenon in some depth, since Teflon FEP bags are widely used as reactors, and the uptake of $O_3$ by the bag could alter the course of the reaction. Also, several experimenters have reported the use of Teflon sampling tubes (Gay and Bufalini (1971). Gay and Bufalini (1971), however, have found 93% of the initial nitrogen charge present (in the form of nitrogen-containing compounds) in the gas phase in a trans-2-butene-$NO_x$ experiment carried out in a Teflon FEP reactor. They suspect that Teflon might have a lower adsorption rate for oxides of nitrogen than does glass, but this observation is based on a single run.

Clearly, an optimal surface material must be identified before further expensive smog chamber studies are carried out. The best material will be the one showing the lowest loss rate for each pollutant individually (i.e., NO, $NO_2$, $O_3$, various hydrocarbons, aldehydes) and collectively (i.e., under irradiated smog chamber conditions). Furthermore, it will be necessary to determine quantitatively the loss rate for each pollutant once a material has been selected.

### b. Surface to Volume Ratios

The effect of surface to volume ratio on smog chamber experiments has been largely ignored in the past. In a recent study, however, Sabersky et al. (1973) found that the ozone decay rate in their chamber was directly related to the surface to volume (S/V) ratio. Certainly, increasing the S/V will in turn increase the probability of a given molecule striking the surfaces. Thus, other factors being equal (e.g., concentrations, wall conditions, mixing rate, etc.), a reduction in the ratio will lessen surface effects.

Ideally, the S/V ratio should be as close to zero as possible. Unfortunately, problems other than those associated with surface effects arise in using large chambers. Thus, we must set as a goal the understanding of the effects of S/V ratio on smog chamber experiments, so that we can correct or otherwise compensate for them (rather than eliminate them). In his current study, Jaffe (1972) plans to compare chamber results using two different S/V ratios for the same initial conditions. In principle, identical chamber runs should be performed at four or five S/V ratios. Also, baffling or other packing (e.g., turnings) of the same composition as the walls can be added to the chamber to evaluate the effect of increased surface area.

### c. Cleaning and Preparation of the Surfaces

In order to obtain reproducible results from a chamber, the chamber surfaces must, among other things, be brought to a known initial condition. Several techniques have been used with varying degrees of success. The most common technique of cleaning a chamber between runs, especially a large environmental chamber, is simply to force filtered laboratory air through the chamber with lights on and fans running either overnight or until no more pollutants are detected by the monitoring equipment. Unfortunately, this technique does little to remove the adsorbed materials from the walls of the chamber.

A second technique is to evacuate the chamber using a vacuum system. This is an efficient way of removing the bulk gas, especially for small chambers. Removal of material from the walls would require several days of pumping unless the walls were heated to drive off the water and other species. Under these conditions, pumping would only require several hours. The cleaning efficiency of this technique, however, remains to be assessed.

A method used by some experimenters for cleaning the surfaces involves allowing high levels of ozone, for example, 20 to 40 ppm, to react with materials on the walls of the chamber for several hours. This procedure results in complete oxidation of all substances which will react readily with ozone, but it does not remove any of the oxidation products from the walls.

A technique reported by Gay and Bufalini (1971) for cleaning of the walls of a small (72 liter) boro-silicate glass reactor involves washing the surfaces before each irradiation with aqueous cleaning solution, acetone, and finally with distilled water (the latter, several times). This is the surest way of removing material from the surfaces, but it is a time-consuming, manual task that is unsuitable for larger environmental chambers. Whatever surface material is chosen for future chambers, it will be necessary to evaluate the various methods of cleaning the surfaces. At this time it appears that the three-stage washing technique of Gay and Bufalini is preferable to other suggested procedures.

Independent of the relative degree of success or failure of each of these cleansing techniques, there remains some question as to whether "the cleanest surface is the best." Sabersky et al. (1973) found that the decomposition rate constant of ozone on Lucite decreased by 50% over the first eight hours of the material's exposure and then continued to decrease slowly as the chamber "aged". The same general trend was observed for neoprene (70% decrease in the rate constant in the first 100 minutes of exposure). These results suggest that clean walls can be partially deactivated by intentionally exposing them to ozone. Surfaces of metal-walled chambers become deactivated as an oxide layer forms at the air-wall interface. If the oxide layer remains intact after cleansing, the cleansing procedure might well result in a stable and reproducible surface condition.

### d. Effect of Adsorbed Water on Wall Reactions

Even in so-called dry systems it is reasonable to assume that an adsorbed layer of water will be found on the walls of the chamber. This would certainly be the case in experiments run under ambient conditions with 25-75% relative humidity. Although little attention has apparently been paid in the past to carefully controlling the relative humidity in smog chambers, there is reason to believe that the amount of water in a chamber markedly affects the rate of loss of pollutants to the surfaces.

In one set of experiments Cox and Penkett (1972) found that a three-fold increase in the relative humidity (from 30% to 86%) resulted in a 35-fold increase in the first order decomposition rate constant (from 0.00425 $\text{min}^{-1}$ to 0.139 $\text{min}^{-1}$) of $SO_2$ on a gloss paint surface. In examining the decomposition of ozone on aluminum surfaces they found that increasing the relative humidity from 32% to 83% resulted in a three-fold increase in the first order loss constant, from 0.0038 to 0.0112 $\text{min}^{-1}$. They accounted for the degree of mixedness of the system in their calculations, but because of their experimental method, they were forced to add NO to the ozone system prior to the experiment to prevent aerosol formation from occurring. Since NO reacts rapidly with ozone and since experimental data collected are based upon a single determination, the $O_3$ loss data should be scrutinized carefully. Nevertheless, the substantive effect of variations in relative humidity on the loss rate of $SO_2$ and $O_3$ seems to be clearly established in this work. In related work Mueller et al. (1973) has found that the decomposition rate constant of ozone on aluminum is greatly influenced by the relative humidity. Sabersky et al. (1973), however, found the rate constant for ozone loss on Lucite to be little affected by humidity over a range of 15% - 90% RH. This effect is, as of yet, unexplained, although it may be a function of surface material, the temperature of the surface, and consequently, the amount of water on the surface.

The most direct way in which water can serve as a scavenging agent for the chamber pollutants is through the dissolution of the gases in the adsorbed water layer on the walls. In examining vegetation as a sink for atmospheric pollutants, Hill (1971) demonstrated a relationship between the absorption rate and the solubility in water of each pollutant he studied. In particular, $SO_2$ is very soluable in water (39.4 cc/cc $H_2O$ at $20^oC$), $O_3$ is slightly soluble (0.26 cc/cc $H_2O$), and NO (.05 cc/cc$H_2O$) and CO (.02 cc/cc $H_2O$ are much less soluble. The loss rate data for $SO_2$ and $O_3$ collected by Cox and Penkett (1972) confirm this general trend. Although Gay and Bufalini (1971) did not investigate the problem of $NO_2$ adsorption in detail, they found that when they irradiated 6 ppm of $NO_2$ for four hours in air about 10% of the initial $NO_2$ was adsorbed on the walls, hydrolyzing to equal amounts of nitrate and nitrite,

$$6NO_2 + 3H_2O \rightleftarrows 3HNO_3 + 3HNO_2$$

$$3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O$$

We have not found chamber adsorption data for NO or CO.

One pollutant not included in the solubility table found in Hill (1971), but which forms in significant quantities after the $NO_2$ peak, is $N_2O_5$, the acid anhydride of nitric acid.

This species hydrolyzes readily by the reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

Gay and Bufalini (1971) have suggested that this is the major source of nitrate on the walls. To test the hypothesis they performed two experiments. Knowing that $N_2O_5$ forms by the reactions:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \rightleftarrows N_2O_5$$

they first introduced 6 ppm of $NO_2$ and 1.6 ppm of $O_3$ into a 72 liter glass reactor and allowed them to react for four to six hours. Gas phase analysis did not indicate the formation of nitrate, but washing the walls with a basic solution yielded 3.1 ppm of nitrate and 0.1 ppm of nitrite. (The stoichiometry of the above reactions suggests that a maximum of 3.2 ppm of nitrate would form if all the $O_3$ reacted with $NO_2$). In the second experiment they introduced vaporized nitric acid into their reactor. After three hours nearly all of the nitric acid was still confined to the gas phase. These experiments strongly suggest that $N_2O_5$ is adsorbed and hydrolyzed on the walls of the reactor rather than hydrolyzing in the gas phase and then diffusing to the surfaces as nitric acid.

The literature concerning the effect of water on the photo-oxidation rate of hydrocarbons has been reviewed recently by Altshuller and Bufalini (1971). Although various investigators have seen some increase in reactivity when water was added to an experimental system, Altshuller and Bufalini attributed these observations to changes in the reactivity of walls. Presumably, water can deactivate surface sites on a wall with the consequence that free radicals are longer lived. This hypothesis is worthy of further inquiry.

In the future investigators should attempt to estimate the amount of water on the surfaces of smog chambers. One should expect that the quantity of water will depend both upon the relative humidity in the system and the temperature of the walls. Wall uptake studies should also be performed for individual gaseous pollutants to assess the rate of loss of these species to the walls under various typical experimental conditions. It now appears that $N_2O_5$ and $SO_2$ are strongly affected by the amount of water on the walls, $O_3$ and $NO_2$ are affected to a moderate degree, and based solely on solubility data, NO and CO may be affected the least. Data for the interaction of aldehydes and the various class of hydrocarbons with water-covered surfaces remain to be determined.

### e. Effect of Temperature

In chapter IV we noted that several investigators have observed the rate of smog formation to accelerate when the operating temperature of a chamber is raised. We presented as one possible explanation the fact that the majority of reactions contributing to smog are thermal, and for the most part, will proceed somewhat faster at higher temperatures. It is not presently known, however, if this effect is sufficient to explain completely the effect of changes in temperature on the rate of smog formation. Dimitriades (1967) has suggested that surface effects might change with the temperature of the walls. For example, water evaporates from the surfaces as their temperature increases, potentially exposing more reactive sites and decreasing the probability of pollutant loss by dissolution in the water layer and by heterogeneous hydrolysis. The effect of temperature on surface effects might be determined by repeating an identical smog chamber experiment at a constant air temperature but with heated and/or cooled walls. If no change in the rate of smog formation were observed, the effect of temperature could be attributed entirely to changes in the rates of the thermally-induced elementary reactions. Otherwise, surface effects must be determined as a function of temperature, so that proper compensation can be made when interpreting the data.

### 3. Radiation Simulation

The principal driving force in the smog reaction system is the photolysis of $NO_2$:

$$NO_2 + h\nu \xrightarrow{k_1} NO + O.$$

Although there are other absorbing species present in the atmosphere (e.g., peroxides, aldehydes), these are not considered "driving forces" as either they are found at low concentrations relative to $NO_2$ or their photolysis rates are low. As a result, the rate of photolysis of $NO_2$, $k_1$, can serve as a useful measurement of the ultraviolet light intensity. Because of the importance of this photo-initiation reaction to the overall smog kinetics,* the measurement of the spectral distribution, spatial intensity distribution, spatial intensity distribution, and absolute intensity of the radiation are extremely important. If they are not determined with care, one can neither meaningfully compare experiments performed in different chambers, nor extract quantitative information from an individual experiment.

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* The sensitivity of the smog formation rate to $k_1$ is demonstrated in a computer simulation of the n-butane/toluene/$NO_x$ system (Hecht, 1972). Using a base value of $k_1 = 0.266$ $min^{-1}$, the $NO_2$ peak occurred at 112 minutes. Decreasing $k_1$ to 0.166 $min^{-1}$ resulted in a time to the $NO_2$ peak of 169 minutes; increasing $k_1$ to 0.366 $min^{-1}$ resulted in a time to the $NO_2$ peak of 84 minutes.

### a. Artificial Irradiation

Tuesday (1961) has shown that the spectral distribution of fluorescent lamps centered at 3550A is somewhat different than that of the ultraviolet spectrum of the sun. A question then arises as to whether these differences significantly affect the course of photochemical smog formation. Laity (1971) studied this problem by comparing product concentrations observed after irradiation of several synthetic smog mixtures by blacklight fluorescent lamps with concentrations observed when identical mixtures were irradiated using natural sunlight. (In this study it was not necessary for the output of the lamps to remain constant in intensity, for the results were compared with those obtained for irradiation by sunlight, which varied in intensity over the course of the experiment. In chamber kinetic studies, however, it is important that the intensity be constant or, at least, well defined). He found no significant discrepancies between comparable mixtures over the period of the irradiations, thereby justifying the use of blacklight fluorescent lighting in smog chamber studies.

While the output of lamps undergoes a natural deterioration with age, a process accelerated by operating the lamps at an overvoltage, a critical factor in stabilizing the UV output of the black-light fluorescent lamps is that the operating temperature of the lamps be kept constant (Dimitriades, 1972). Holmes et al. (1973) report that a rise of 30°F in the temperature of the air surrounding the lamps results in a 40% decrease in the UV output. Because temperature increases of this magnitude are not uncommon in smog chambers, these results highlight the importance of placing the lamps outside the chamber where they can be maintained at a constant temperature by forced air cooling. Outside installation of the lamps, however, introduces the additional constraint that at least portions of the chamber walls be transparent to UV radiation, thereby restricting the choice of surface materials.

### b. Distribution of Light Intensity

Since variations in light intensity at various locations within the chamber result in differing rates of $NO_2$ photolysis, hence, of smog formation, it is vital that the radiation be uniform throughout the chamber. Often, lamps are located on one or two sides of cylindrical or box-shaped chambers. Because intensity is inversely proportional to the distance from long cylindrical lamps, such a configuration can lead to intensity gradients in the chamber. It should be noted that Niki (1973) has built a cylindrical chamber of glass with lamps placed in a geometric configuration about the reactor such that the maximum variation in intensity in the chamber is no more than 5-10%. Thus, the existence of intensity gradients in chambers need not be accepted as an inevitable consequence of a particular geometric configuration.

### c. Measurement of Light Intensity

Although it would be desirable to determine the radiation within a chamber by measuring the intensity as a function of wavelength, such an approach requires equipment which is both complex and expensive. Thus, it has become customary in photochemical smog studies to calibrate UV sources by measuring a manifestation characteristic of the light source, namely, the photosis rate of $NO_2$. The rationale for this method is that the fundamental photochemical process in smog formation is the photolysis of $NO_2$

$$NO_2 + h\nu \xrightarrow{k_1} NO + O$$

and that the rate of this reaction determines, to a large extent, the rate of the overall process. The method, first suggested by Tuesday (1961), consists of photolyzing an initial charge of $NO_2$ in an inert atmosphere (e.g., $N_2$) and in some manner determining the first order rate constant for $NO_2$ decay, $k_1$, from the $NO_2$-time data.

Originally, a pseudo first-order decay parameter, $k_d$, was taken as a measure of the light intensity. But because the decay of $NO_2$ in $N_2$ is *not* a first-order process, $k_d$ reflects the combined result of a large number of reactions (see Table 8) rather than the result of just the single reaction 1 . Therefore, $k_d$ is not a fundamental rate constant of the system. When smog chamber data are used for the purpose of validating chemical mechanisms, $k_1$, *not* $k_d$, must be specified.

Holmes et al. (1973) have shown that $k_1$ can be determined directly from the $NO_2$-time data obtained by irradiating $NO_2$ in dry, oxygen-free nitrogen. One simply notes the initial ($[NO_2]_o$) and final ($[NO_2]$) concentrations of $NO_2$ and the length of photolysis ($\Delta t$), $k_1$ is then determined from the following equation;

$$k_1 = \frac{1}{2\Delta t}\left\{(1 + R_1 - R_2)\ \ln\frac{[NO_2]_o}{[NO_2]} + R_2\left[\frac{[NO_2]_o}{[NO_2]} - 1\right]\right\} \qquad (34)$$

$$R_1 = 0.27$$

$$R_2 = 0.16$$

TABLE 8. Reactions and Rate Constants for the Photolysis of Nitrogen Dioxide in $N_2$ and $O_2$

| No. | Reaction | Rate Constant | Reference |
|---|---|---|---|
| 1. | $NO_2 + h\nu \rightarrow NO + O$ | To be Estimated | |
| 2. | $O + O_2 + M \rightarrow O_3 + M$ | $2.33 \times 10^{-5}$ ppm$^{-2}$ min$^{-1}$ | Johnston (1968) |
| 3. | $O_3 + NO \rightarrow NO_2 + O_2$ | $2.95 \times 10^{1}$ ppm$^{-1}$ min$^{-1}$ | Johnston and Crosby (1954) |
| 4. | $O + NO_2 \rightarrow NO + O_2$ | $1.38 \times 10^{4}$ ppm$^{-1}$ min$^{-1}$ | Schuck et al. (1966) |
| 5. | $O + NO_2 + M \rightarrow NO_3 + M$ | $4.50 \times 10^{-3}$ ppm$^{-2}$ min$^{-1}$ | Schuck et al. (1966) |
| 6. | $NO_3 + NO \rightarrow 2\ NO_2$ | $1.48 \times 10^{4}$ ppm$^{-1}$ min$^{-1}$ | Schott and Davidson (1958) |
| 7. | $O + NO + M \rightarrow NO_2 + M$ | $2.34 \times 10^{-3}$ ppm$^{-2}$ min$^{-1}$ | Kaufman (1958) |
| 8. | $2\ NO + O_2 \rightarrow 2\ NO_2$ | $7.62 \times 10^{-10}$ ppm$^{-2}$ min$^{-1}$ | Glasson and Tuesday (1963) |
| 9. | $NO_3 + NO_2 \rightarrow N_2O_5$ | $4.43 \times 10^{3}$ ppm$^{-1}$ min$^{-1}$ | Schott and Davidson (1958) |
| 10. | $N_2O_5 \rightarrow NO_3 + NO_2$ | $1.38 \times 10^{1}$ min$^{-1}$ | Mills and Johnston (1951) |
| 11. | $NO_2 + O_3 \rightarrow NO_3 + O_2$ | $1.06 \times 10^{-1}$ ppm$^{-1}$ min$^{-1}$ | Johnston and Yost (1949) |

The validity of this equation was established both through experiments in a long path infrared spectrometer cell and through computer simulation of the "Ford-Endow" mechanism (Ford and Endow, 1957) for the reactions taking place in the $NO_2$-$N_2$-light system (see Table 8). Since one can obtain $k_1$ directly via this procedure, we suggest that future investigators use $k_1$ rather than the pseudo-first order decay constant for $NO_2$, $k_d$, to characterize UV intensity in photochemical smog experiments.

It is impractical or impossible to purge and fill large environmental chambers with a $NO_2/N_2$ mixture. Rather, one can formulate the $NO_2/N_2$ mixture in a semi-transparent Tedlar bag and irradiate it for a short period, determining both the initial and final $NO_2$ concentrations. Equation (34) can then be used to calculate $k_1$, although a correction must be made for transmission by the Tedlar. Such a technique is used by California Air Resources Board investigators in establishing $k_1$ for experiments carried out in their 1100 $ft^3$ chamber (Holmes et al., 1973).

Determination of the light intensity in an outdoor chamber is a more difficult problem, as it is impossible to control the intensity of the sunlight. (In his study Laity (1971) found that "$k_d$" outdoors varied between 0.15-0.30 $min^{-1}$ depending on the day and time.) Consequently, it is necessary to determine $k_1$ several times during the course of a run, and particularly, to note any abrupt changes in the light intensity. In view of Laity's results showing that fluorescent lamps produce the same results as sunlight for comparable experiments and the fact that it is impossible to control the intensity of natural sunlight, *there does not appear to be any advantage in performing outdoor smog chamber studies if kinetic information is being sought.*

Because it is difficult to remove all the $O_2$ from the system, as is required in determining $k_1$ by the procedure just described, it would be useful to develop a means for determining $k_1$ in air. We devote Appendix A to a discussion of a general method by which $k_1$ can, in principle, be determined directly and accurately from the $NO_2$ concentration-time data observed when an arbitrary mixture of $NO_2$ and NO (if any) is photolyzed in air. The essential feature of the method is that a computer estimation algorithm (presented in the appendix), rather than a simple expression such as (34), is required to determine the value of $k_1$.

## 4. Summary

While it would be desirable to develop and design an entirely new smog chamber after techniques have been developed for reducing chamber effects, consideration of such an approach must be tempered by an evaluation of costs and development time involved. Failing the development of a new chamber, it is necessary to establish quantitatively in an existing chamber:

- the completeness of mixing
- the interactions between the surfaces and the gas phase chemistry, and
- the uniformity and intensity of the artificial irradiation.

Furthermore, particular effort must be made to establish material balances during smog chamber irradiations. If smog chamber data are to be used for validating kinetic mechanisms, no variable associated with the smog chamber system that can potentially affect the outcome of the photochemical process should be ignored or overlooked. All such variations must be monitored and reported.

## B. Analytical Procedures

The usefulness of reproducible smog chamber data ultimately depends to a large degree on the reliability and completeness of the chemical measurements. Five species, namely $NO_2$, NO, $O_3$, hydrocarbons, and aldehydes, are the most important reactants in smog and, with the exception of aldehydes, have generally been measured in chamber experiments. In this section we examine alternative analytical techniques that may be used in determining the concentrations of these five species. There are, however, many other species present in smog (such as peroxides and nitric acid) which one might wish to monitor, both to elucidate the mechanism of smog formation and to validate kinetic mechanisms. These species are discussed in part c of this section.

Analytical instruments fall into two classes. The first class includes instruments which may be used to make a direct measurement for some *physical* property of the species under observation. An example of such an instrument is the infrared spectrometer, which detects the amount of infrared radiation absorbed by specific pollutants. The second class of instruments, and by far the most common, is the chemicophysical. In this case the pollutant being measured first undergoes chemical transformation; the product of the reaction is then measured using an appropriate analytical technique. As an example, the classical "wet" chemical techniques are all chemicophysical. In these, a sample of the pollutant is collected for a period of time in a liquid absorber. The sample is then reacted with another reagent, resulting in a change in color or in the formation of another product. The intensity of the color or the concentration of the products are related to the concentration of the original pollutant. Many newer types of instrumentation, such as chemiluminescent devices (which are based on measuring the light emitted when the pollutant being monitored reacts with another reagent), are also chemicophysical.

A number of criteria may be specified for evaluating the appropriateness and utility of an analytical technique for a particular application. These include:

1. the accuracy, specificity, and ease of calibration of the instrument
2. the precision or reproducibility of the measurements
3. the volume of gas required to make a determination
4. the response time of the instrument.

In the discussion that follows, we first examine these criteria individually. We then use them in evaluating the quality of measurements to be expected from analytical instruments which either have been employed extensively in the past, or have recently been developed, to measure $NO_2$, NO, $O_3$, hydrocarbons, and aldehydes.

1. Accuracy and Primary Standards

The accuracy of a method, that is, the extent to which the observed or measured value and the "true" value agree, depends on both the specificity of the technique and the accuracy of calibration. Lack of specificity, or the presence of interferences due to species other than the one desired, is the greatest shortcoming of all wet methods. For example, in the measurement of ozone by the potassium iodide (KI) method (see part 5 of this section), peroxides, $NO_2$, and peroxyacylnitrates, in addition to ozone, will all give a positive response, while $SO_2$ and dust give a negative response relative to the value observed without the interference. Thus, the accuracy of the indicated $O_3$ concentration is, at best, questionable when these other species are present.

The accuracy of calibration procedures depends upon the availability of primary standards. The well-established wet chemical techniques fare very well in this regard (Katz, 1968), while suitable primary standards are still being sought for many of the gas phase monitoring techniques. For instance, as of yet no primary standard for $O_3$ has been developed, and ozone sources such as air ozonizers must be calibrated by potassium iodide titration or other techniques before each use as an ozone source. Nitric oxide and many hydrocarbons, on the other hand, can be obtained in prepurified gas cylinders and can thus serve as precision gas standards for those species.

Recently, O'Keefe and Ortman (1966) developed permeation tubes as calibration standards. They found that liquified gases, such as $SO_2$, $NO_2$, and hydrocarbons, sealed in Teflon tubing, would permeate through the walls of the tubing at a constant rate which is dependent upon the surface area of the tubing and the temperature of the surroundings. The success of this technique depends on the fact that the equilibrium vapor pressure of a liquid is a constant when temperature is held constant. Under these conditions, the permeation rate of the gas through the tube is constant, and the absolute amount of gas released by the tube over a period of time can be calculated from the change in weight of the tube. Permeation tubes have been used successfully for $SO_2$, $H_2S$, many hydrocarbons, anhydrous $NH_3$, anhydrous HF, $COCl_2$ (phosgene), and organic mercury compounds (c.f. Saltzman et al., 1971). Unfortunately, it has been found that $NO_2$ permeation tubes are seriously affected by relative humidity and the past history of exposure (Saltzman et al., 1971). Thus, permeation tubes for $NO_2$ are not suitable as a primary standard unless they have been recently calibrated.

The frequency of recalibration must be established for each instrument in the laboratory. Loss of calibration can occur as a result of aging and decomposition of chemical reagents or because of changes in ambient operating conditions (i.e. temperature, relative humidity, pressure). The need for recalibration will also depend on the sensitivity of the plumbing, the stability of the electronic components, and the conditions under which the instrument is used. Recalibration should be performed sufficiently often to assure the accuracy of the results. Any observed drift between calibrations should, of course, be noted. Finally, the calibration experiments should be performed over the full concentration ranges of the species observed during an experiment (e.g., for $NO_2$, concentrations vary from 0.005 ppm to 2 ppm).

## 2. Precision

Precision refers to the extent to which a given set of measurements agrees with the mean of the observations. Although, the precision of each instrument must be determined individually, it has been found, in general, that both wet chemical techniques and instrument-based techniques such as chemiluminescence produce highly reproducible results (Maugh, 1972). It is, of course, important that the precision of the measurements be reported with the results. Care should be taken to establish the precision as a function of concentration. Photochemical simulation studies have shown that the predicted time to the $NO_2$ peak can be shifted by 15 minutes or more because of uncertainties of ±.02 ppm in an initial $NO_2$ concentration of .04 ppm (Hecht, 1972). Thus it is particularly important to know precision bounds at low $NO_2$ concentrations if the predictions of kinetic mechanisms are to be correctly evaluated.

3. Sampling Procedures

The reliability of a measurement depends to a large degree on the technique used to sample the bulk gas. Presumably, a representative sample can be drawn from any location within a well mixed reactor. The sampling tube material should be selected to minimize the heterogeneous loss of pollutants during sampling. Further, the residence time in the sampling line should be as short as possible to minimize the possibility of chemical reaction along the path. The overall accuracy of a measurement will depend upon careful calibration of the air flow rate into the monitoring equipment, for the signal output of the instrument must be corrected for the total volume of gas being determined. Calibrated low capacity rotameters can be used to measure low air sampling rates, while very high volumetric flow rates can be calibrated more accurately with such devices as Venturi meters or Pitot-static tubes.

One final consideration related to sampling is that it is desirable to minimize the total volume of air required for the analytical instruments so as to minimize the loss of reactants from the smog chamber. It is not uncommon for up to 25% of the initial reactants to be removed from a moderate sized chamber (10,000 liters) through sampling over a six hour irradiation . Such removal can be reduced substantially by using newer measurement techniques, such as chemiluminescence, which requires samples no larger than a few cubic centimeters. (Older wet methods often require that many liters of gas be bubbled through a concentrating solution before a reading can be made). In any case it is important to report the dilution rate in the experiments so that corrections for losses can be made.

### 4. Response Time

In smog chambers in which the concentrations of pollutants are changing continuously, knowledge of the response time of the measuring systems is necessary for interpreting the data relative to real time. Response time is the time from the moment the pollutant enters the sampling instrument to the moment that the measured value is obtained. The measured value, in turn, is taken to be a specified percentage of the final or true value, such as 90%. Thus, if it requires two minutes to achieve 90% of full response, two minutes is the response time. For systems in which the sample lag time is great Mage (1972) and Schnelle and Neely(1972) have shown that the transient and frequency response of the instruments can be accounted for by use of a transfer function.

Measurements carried out using instrumentation employed in chamber work are generally made either on a continuous, discrete, or averaged time basis. The first and most desirable type of measurement is *continuous* and is carried out using instruments with very fast response times, such as infrared spectrometers. A second class of measurements, *discrete*, includes those analyses in which a sample is injected into the instrument. Gas chromatographic analysis is an example of a discrete procedure. The sensitivity of discrete measuring instruments to short-term fluctuations and sharp peak concentrations will depend upon the rapidity with which determinations can be made. In the limit, as the time between measurements goes to zero, discrete measurements, of course, become the same as continuous measurements. Monitoring devices which require a pollutant to be collected over a finite period of time in order to obtain measureable concentrations yield *integrated* or averaged results. Most wet techniques operate on this principle. Such methods, of course, suffer from the obvious disadvantage that they are insensitive to short-term variations in concentration. Thus, wet chemical techniques, which require a ten minute or longer sampling time, will represent a sharp $NO_2$ peak as a lower and broadened peak because of their slow response times (and, thus, low time resolution).

### 5. Analytical Techniques Available for Measuring The Pollutants

Because of the wide variety of analytical instruments presently available for monitoring the constituents of smog, there is often uncertainty concerning which procedures are "best". Although recommended procedures are published regularly by the U.S. government in *The Federal Register*, review articles on current trends in instrumentation suggest that techniques now in use will soon be replaced by more rapid, more reliable, more efficient and certainly more expensive techniques (Maugh, 1972). A logical goal in upgrading analytical devices would be to develop a single instrument capable of measuring many or all of the pollutants simultaneously. Microwave spectrometers, which measure the rotational energy of polar molecules at discrete frequencies, appear promising in this regard, but commercial availability is at least two years away (Maugh, 1972). Because of the uncertainties concerning analytical procedures, it is worthwhile to examine briefly the techniques most often used to measure the standard pollutants ($NO_2$, NO, $O_3$, HC's, aldehydes) and to discuss the advantages and disadvantages of techniques now becoming available.

#### a. $NO_2$

Nitrogen dioxide has generally been determined by the Saltzman method (Saltzman, 1954).

In this technique the sample is bubbled through an absorbing reagent at a rate of about 0.4 liter/minute for 10 minutes in order to concentrate the $NO_2$. Reaction of $NO_2$ with the absorbing solution results in a color change which can be related to the $NO_2$ concentration. The technique is quite reproducible but suffers interferences from ozone and PAN (Leithe, 1970). The primary sources of error in this method are chemical interferences, inefficiency of collection, and the aging of reagents.

No substantial improvement over the Saltzman method has, as yet, been made for determining $NO_2$. Hodgeson et al. (1972) have suggested reducing the $NO_2$ to NO using "carbonized sugar" or glass wool as a catalyst and measuring the resulting NO by chemiluminescence (see paragraph 5b). The problem with this approach is that the catalyst will reduce all the higher oxides of nitrogen (i.e. nitrates, PAN, nitrite, $NO_2$) to NO, so the technique lacks specificity. One promising approach for measuring $NO_2$ which is currently being developed involves exciting $NO_2$ to a higher energy state with a tunable dye laser. The $NO_2$ concentration can then be determined by measuring the fluorescence of the excited molecules (Nader, 1972).

### b. NO

Until recently, there was no available technique for determining nitric oxide concentrations directly. The pollutant gas was passed over an oxidizing agent such as dichromate which oxidizes NO to $NO_2$. Total oxides of nitrogen were then determined as $NO_2$ by the Saltzman method, and NO was calculated by subtracting the $NO_2$ reading made at the same time from total $NO_x$. In addition to all the difficulties involved with the Saltzman method, the technique depends on the efficiency of oxidation of NO. Efficiencies of only 70 - 85% were not uncommon, and thus measurements of NO made by this method were unreliable (Tokiwa and Mueller, 1971).

Recently Stedman et al. (1972) and Hodgeson et al. (1972) have shown that NO can be determined very accurately by chemiluminescence. In this technique the pollutant sample is exposed to a large excess of ozone. The ozone reacts rapidly with the NO to form $NO_2$ in an excited state.

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

Collapse of the excited $NO_2$ to the ground state is accompanied by the emission of light, which is then measured and related to the initial NO.

$$NO_2^* \longrightarrow NO_2 + \text{light}$$

This technique is sensitive to $10^{-3}$ ppm of NO, has an overall response time of ten seconds, and requires a flow rate from the chamber of only 20 cc/minute. Interferences can be caused by collisional deactivation of the excited $NO_2$ (this problem is reduced by operating the system at low pressures) and by the reaction of other species present with $O_3$, the product of which will also chemiluminesce. Stedman et al. investigated the possibility of interferences from $SO_2$, $NO_2$, $Cl_2$, $H_2O$, $CH_4$, $C_2H_2$, $C_2H_4$, and $C_3H_6$ at a concentration of 100 ppm in air, but found that these species did not emit a detectable amount of light in the region of the $NO_2^*$ luminescence. An interesting feature of this instrument is that it can be used as an ozone detector as well by subjecting an air sample to an excess of NO. In view of its accuracy, response time, sensitivity, stability, and versatility, this instrument shows great promise for the future.

c. $\underline{O_3}$

Traditionally, ozone determination has been based on reaction of the species with potassium iodide (KI)

$$2\ KI + O_3 + H_2O \rightarrow I_2 + O_2 + 2\ KOH$$

and measurement of the amount of iodine which is liberated by the reaction. Under well controlled laboratory conditions, this method can be quite accurate, and the technique remains as one important method for calibrating ozone sources. However, automatic monitors for ozone based on the KI reaction suffer from numerous difficulties. Several species, including $NO_2$, peroxides, and PAN, give a positive response for $O_3$ in varying degrees, while the presence of $SO_2$ and reducing dusts result in a serious negative interference (Katz, 1968). Although some of the interfering species such as $SO_2$ can be removed by chemical scrubbing before the pollutant gases reach the ozone monitor and others can be corrected for mathematically (e.g., $NO_2$), the KI method must be regarded, at best, as a method for determining the total *oxidant* concentration in a smog chamber. An additional difficulty with the method is that the oxidant must be collected in a concentrating solution by bubbling gas from the chamber at the rate of 1-2 liters per minute for 15 minutes; full development of the color requires an additional 30-60 minutes. Thus, in summary, the KI method provides a non-specific, averaged oxidant concentration with poor response time.

Two techniques have recently been developed as commercial products for determining ozone. The first method is based on the chemiluminescence of the ozone-ethylene reaction (Warren and Babcock, 1970). An air sample containing ozone is exposed to a large excess of ethylene in a reaction vessel. The light released during the reaction is then measured using a photomultiplier tube and related to the ozone concentration.

Ozone can be determined by its chemiluminescent reaction with many species besides ethylene. We have already mentioned that the reaction of $O_3$ with NO has been used successfully by Stedman et al. (1971). Recently, Kummer et al. (1971) have pointed out that ozone will undergo chemiluminescent reactions with many olefins and sulfides including tetramethylethylene and dimethylsulfide, and that these reactions result in a much greater intensity of emitted light than the ozone-ethylene reaction.

Chemiluminescent methods for ozone appear to be free of interferences from other species present in smog, and they are sensitive and fast. However, they suffer the disadvantage of having to be operated at very low pressures in the reaction vessel (0.5-5 Torr). Tanks of gaseous reagents must also be used in operating the equipment.

The second technique marketed recently measures the ultraviolet absorption of ozone in a sample of polluted air (Bowman and Herak, 1972). The air is divided into two portions in the instrument. One portion passes over a catalyst which converts the ozone to oxygen and becomes the reference gas, while the other portion is untreated. Ozone concentration is then calculated from the difference in UV absorption of the two samples. The referencing technique has the advantage of minimizing interference from moisture and other pollutants, since they are present in equal amounts in each sample, and the differencing method ideally produces a net signal of zero. Because the source of the UV light is a mercury vapor lamp, mercury contamination in the air can provide a serious interference. The mercury can be eliminated, however, with a gold surface absorber placed at the sample inlet. Another potential source of interference is the presence of any molecules which absorb ultraviolet radiation, such as $SO_2$ and aromatics. However, tests conducted at concentration levels of 0.2 ppm of $SO_2$ and 1.00 ppm of benzene showed no detectable response. The instrument is sensitive to 0.001 ppm, has an accuracy of ±3%, precision of ±1%, and has a response time of 30 seconds (90%). One negative feature of the instrument, when it is to be used for chamber studies, is that it requires a flow rate of 3 liters/minute; thus, it is not suitable for continuous monitoring in small chambers.

### d. Hydrocarbons

Measurement of the concentrations of individual hydrocarbons cannot be made until the hydrocarbons are separated from the other pollutant gases and from each other. This is in contrast to the requirements placed on analytical procedures employed in the measurement of $NO_2$, NO, and $O_3$, which involve the use of an unrefined sample of bulk gas. Gas chromatography has been applied very successfully for separating hydrocarbons. With appropriate choice of columns (see Altshuller, 1968) and a flame ionization detector, paraffins having carbon content of up to at least $C_6$, olefins up to at least $C_6$, aromatics in the $C_6$-$C_{11}$ range, and acetylenes can be resolved and measured accurately. The principal drawbacks of GC analyses are the time required to separate a sample and the complexity and maintenance requirements of the measurement. Although discrete samples are analyzed, the cycling time is much too large to approximate continuous monitoring. Unfortunately, no significantly better techniques for measuring individual hydrocarbons than gas chromatography have yet been suggested.*

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* Total hydrocarbon analyses of samples from the bulk gas can be made directly using a flame ionization detector; total non-methane hydrocarbons can also be determined by difference if the methane is separated from the gas with an activated charcoal column and determined individually. Because of the complexity of the hydrocarbon mixture and the fact that all carbon-containing molecules give a response, these measurements contribute little to elucidating the state of the system.

### e. Aldehydes

No satisfactory method exists at this time for measuring individual aldehydes. Total aldehydes have been determined in chambers using both infrared spectrometry and wet chemical techniques. Wet chemical techniques based on the use of chromotropic acid or other reagents have been employed to measure formaldehyde, but these methods suffer from several types of interferences (e.g., olefins and aromatics) (Altshuller, 1968). Some progress has been made by Seizinger and Dimitriades (1972) in separating and identifying aldehydes by gas chromatography, but the technique is still cumbersome and time consuming. Again, we are not aware of any current improvements being made for the rapid measurement of individual aldehydes.

## 6. Summary

The shortcomings of analytical techniques based on wet chemical methods are very serious, notably a general lack of specificity and poor response time. Newer techniques, based upon chemiluminescence and determination of the spectral properties of various molecules, have already been shown to provide rapid, accurate, and continuous measurements of NO and $O_3$ at low concentrations. In the future these techniques should be used for monitoring smog chamber experiments. There is still a need, however, to develop rapid and accurate analyzers for $NO_2$, hydrocarbons, and aldehydes.

Even with the appearance of the newer instruments, the quality of the data will depend upon the extent to which the instrumentation is properly calibrated and maintained. The experimenter must recalibrate each instrument sufficiently often to guarantee the accuracy of the observed data; the degree of maintenance required will depend on the stability of the components of each instrument and the conditions of use.

Permeation tubes and standard precision gases can be used as primary standards for many gases, but a primary standard for ozone is still not available.

## C. Recommended Smog Chamber Studies

Our discussion thus far has been limited to an examination of the operational aspects of a smog chamber. Once a system is operating reliably and reproducibly, it is possible to perform a large number of simple experiments useful in model verification and mechanism elucidation. In this section we discuss some chemical systems, including both artificial smog mixtures and polluted urban air samples, that might be examined profitably, as well as ways in which smog chambers can be used to assess various atmospheric scavenging processes.

### 1. Simple Hydrocarbon-$NO_x$ Systems

Although hundreds of individual hydrocarbons are present in polluted atmospheres, the majority of the reactive hydrocarbons can be classified as paraffins, olefins, and aromatics. Because each member of a class (e.g., paraffins) tends to react with a given oxidant in a manner and at a rate similar to that of other members of the class, it is possible to approximate crudely the atmospheric hydrocarbon mixture using a simple mixture of a single paraffin, olefin, and aromatic. By further implementing the principles of design in the choice of the initial reactant concentrations for a program of experiments and by measuring the concentration of some of the secondary products with time, it is possible to obtain data that should prove to be very valuable for validating chemical mechanisms.

### a. Hydrocarbons to be Studied

As a prelude to atmospheric validation, it is desirable to demonstrate the validity of a chemical mechanism using smog chamber data based on the reactions of relatively simple hydrocarbon mixtures. Such mixtures, if properly formulated, will simulate actual atmospheric mixtures in terms of the range in reactivity of the individual components and the composition by hydrocarbon grouping. For example, an appropriately chosen mixture of *n-butane, propylene,* and *toluene,* which are assumed to typify paraffins, olefins, and aromatics, respectively, may well be a suitable surrogate. Note that each individual species

1. Constitutes a significant percentage of its class of compounds in polluted atmospheres.

2. Reacts with O, OH, and $O_3$ at rates typical of its respective class.
3. Has been thoroughly studied, both with respect to its elementary reactions with oxidants* of interest and in the more complex reaction environment of the smog chamber.

Any chemical mechanism valid for atmospheric reaction systems must certainly be capable of describing the dynamics of systems composed of species mentioned, individually and in combination. Thus, we recommend a three-stage experimental program. In the first phase each individual hydrocarbon would be studied in a smog chamber over a wide range of $HC/NO_x$ ratios; in the next stage the hydrocarbons would be investigated in pairs; finally, the full three hydrocarbon system would be examined.

### b. Statistical Considerations in Formulating the Initial Conditions

Selection of the initial conditions should be based upon levels of hydrocarbons and $NO_x$ presently observed in the atmosphere and those expected as a consequence of current and future emission abatement programs. Statistical planning of experiments should prove of value in selecting sets of initial conditions that provide the most useful data base, in terms of both information content and ease of analysis. Randomization, factorial and fractional factorial designs, replication of runs, and augmentation of designs should all be considered at the planning stage. See Hunter (1960) and Davies (1960) for further information regarding the statistical design of experiments.

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* An exception is the OH-toluene reaction, for which neither the rate constant nor the mechanism of reaction have yet been determined.

### c. Additional Species Identification and Measurement in the Smog Chamber Useful for Model Validation

As model validation is essentially the process of comparing concentration-time profiles for primary and secondary products predicted by the chemical mechanism with those observed experimentally, the "quality" of a validation effort increases with the number of species monitored. Usually, concentration-time profiles are reported only for hydrocarbon, NO, $NO_2$, and $O_3$. Other species have generally not been followed because specific and accurate analytical methods have not been available for them. While we are aware of the experimental difficulties that such measurements involve, we still believe it is of importance to enumerate species that must eventually be measured if real progress is to be made in model validation. We recommend that the following species be monitored in future chamber studies:

*Aldehydes:* Aldehydes are formed as direct products of some hydrocarbon oxidation reactions and also as products of alkoxy radical decomposition. They begin to appear as soon as the hydrocarbon is oxidized and can accumulate to significant (ppm) levels during smog chamber experiments. Because aldehydes are one of the most important classes of secondary products in smog, the confirmation of kinetics mechanisms' predictions for this species provides an excellent additional check on the accuracy of the mechanisms. For generalized models, the measurement of total aldehydes would be sufficient; for more detailed mechanisms it would be desirable to have separate measurements of at least formaldehyde and acetaldehyde.

*Hydrogen Peroxide:* Hydrogen peroxide has been observed in smog chamber studies and in the atmosphere by Bufalini et al. (1972). It is formed by the recombination of hydroperoxyl

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

radicals, and knowledge of its concentration, along with the rate constant for the recombination reaction (about 5300 ppm$^{-1}$ min$^{-1}$ (Johnston et al., 1970), provides one gauge for estimating the concentration of $HO_2$

radicals. $H_2O_2$ can, of course, photodissociate to form OH radicals, but this reaction is slow, being less than 0.5% of the rate of photolysis of $NO_2$ (Leighton, 1961).

*Pernitrates:* Nitrogen containing species such as PAN represent an important class of secondary products. Measurements of PAN are presently carried out on occasion. We recommend that pernitrates be measured routinely in future chamber experiments.

*Nitric Acid:* Nitric acid currently appears to be the principal sink for nitrogen in the smog system. Little of the $HNO_3$ seems to be present in the gas phase; it forms mainly on the walls and on particles. Thus, continuous measurement of $HNO_3$ is very difficult. These difficulties not withstanding, accurate, continuous analysis of $HNO_3$ would be most valuable.

*Nitrous Acid:* As indicated in Chapter IV, nitrous acid may be present in significant quantities in the atmosphere at sunrise, and also in smog chambers prior to irradiation. Thus, the photolysis of $HNO_2$ may strongly affect the early oxidation rate of hydrocarbons and NO. We recommend that $HNO_2$ be monitored in order to establish the possible importance of this effect as well as to confirm the levels of $HNO_2$ predicted by kinetic mechanisms.

## 2. Controlled Irradiation of Polluted Air Samples from Urban Areas

Because of the number, diversity and complexity of species present in urban atmospheres, the irradiation of simple mixtures may not always be sufficiently representative of pollutant chemistry. It is thus of interest to examine the chemistry of more complex contaminant mixtures. One means for doing this is to charge or "dope" a sample of urban air with a known amount of pollutant and irradiate the mixture in a controlled system. During the 1975 RAPS program in St. Louis some studies of this type are apparently being planned. We recommend that at least four specific doping studies be carried out. For each study an "undoped" or control sample must also be irradiated simultaneously. The experiments recommended are:

1. Raise the CO level in one bag to 25 ppm and irradiate for 8 hours or until sundown, if outdoors. The goal is to assess the effect of low levels of CO on the rate of oxidation of NO and $O_3$ formation in the atmosphere.
2. Add .25 ppm of toluene to one bag. Increased usage of unleaded gasolines in the future will result in greater emissions of aromatics. This experiment is designed to examine that effect.

3. Add .25 ppm of $SO_2$ to one bag. Measurement of the effect of $SO_2$ on $O_3$ levels and on the time to the $NO_2$ peak, as compared with the magnitude of these quantities measured for an undoped sample, is the primary objective.

4. Dilute one bag 25% with clean air. This experiment is designed to study the effect on smog levels of a uniform reduction in all pollutants.

These are a few examples of the kinds of doping experiments that can be performed. Others may also be of interest, such as adding water vapor to one bag, irradiating bags of varying surface roughness, and adding various types of particulates to the bags. The intent of each experiment is to reveal the effect of varying a single parameter on the observed concentration dynamics.

### 3. Controlled Assessment of Natural Scavenging Processes

Surface sinks are one of two broad categories of "ultimate pollutant receptors", aerosols being the other. A number of recent studies indicate that both soils and vegetation take up several of the major pollutants at significant rates. Levy (1970) and Inman et al. (1971) have observed in laboratory studies that nonsterile soils take up carbon monoxide at very rapid rates. Fungi appear to be the organisms involved in the biochemical reactions. Abeles et al. (1971) have reported that hydrocarbons, sulfur dioxide, and nitrogen dioxide react with soil through microbial or chemical means. Vegetation has also been observed to react with atmospheric pollutants. Katz and Ledingham (1939) measured absorption rates of $SO_2$ by alfalfa, and Tingey (1968) has estimated rate of uptake of $NO_2$ by alfalfa and oats. Hill (1971), in a rather extensive study, has rank-ordered major pollutants according to the rate at which they absorb into alfalfa. He observed that $SO_2$, $NO_2$, and ozone were absorbed most rapidly, NO quite slowly and CO not at all. Finally, the more reactive pollutants undergo transformation in contact with materials. Sabersby et al. (1973), for example, have measured relatively rapid ozone decomposition rates on surfaces such as rubber, fabrics, and plastic. The importance of determining rates of losses of pollutants to atmospheric sinks is twofold:

1. It is essential to establishing quantitative methods for estimating losses as a function of a number of variables that influence loss rates.
2. It is essential to completion of material balances over a control volume in the atmosphere.

In general, loss rate for a particular pollutant is related to specific rate of absorption by soil, vegetation, or material, the surface properties of the absorbing substance, concentration of the pollutant in the gas phase, humidity, surface area, surface roughness, and turbulent eddy diffusivity. Also, radiation intensity can influence the rate of absorption by vegetation. To our knowledge, there has been only one attempt to correlate loss rates with these variables through atmospheric observation. Hill (1971) has observed that light intensity, windspeed, height of the vegetative canopy (surface roughness), and pollutant concentration all affect pollutant uptake rates. He has estimated the degree to which changes in a variable influence uptake for particular species--increase in windspeed from one to two mph increases $O_3$ uptake by 50%, increase in height of canopy increases uptake rates about linearly, and increase in $SO_2$ concentration results in a proportionate increase in uptake rates.

The effects of certain influencing variables are best determined in the chamber. For example, specific absorption rates as a function of concentration, temperature, relative humidity, light intensity, and wind speed have been studied under controlled conditions (see Hill, 1971) . Effects of surface properties can also be examined in this way. Eventually, effects of levels of turbulence and degree of surface roughness must be simulated in the laboratory. Studies of this nature, however, are likely to be rather involved and complex.

To summarize, in order to better understand the nature of surface scavenging processes, we recommend that the effects of variables having a significant influence (as delineated in preceding paragraphs) on the specific absorption rates of the major individual constituents of smog by soil, vegetation, and materials (e.g., cement, asphalt, paint, etc.) be quantitatively determined.

## D. Summary

Before smog chamber data can be used to validate photochemical simulation models, the reproducibility and reliability of the data must be established. Thus, successful validation will depend upon the quantitative assessment of all the heterogeneous effects in the chamber, careful measurement of the light intensity over the course of the irradiation, and knowledge of any shortcomings in the analytical measurements.

Reproducibility is a measure of the overall precision in smog chamber experiments. Given identical initial conditions (e.g., concentrations, temperatures, humidity, stirring rates, etc.) the concentration-time profiles of the individual pollutant species should be coincident for runs performed on different days or weeks. Lack of reproducibility may be due to one or more of several possible causes, as discussed earlier in this chapter. First, the activity of the walls may change with time, illustrating the necessity of insuring that the walls are at a known, standard, initial condition before each run. Second, the light sources in the chamber may deteriorate with time. The possibility of this occurring can be examined by measuring $k_1$. Third, the analytical instruments may be out of calibration.

As a good test of repeatability, we suggest carrying out, as often as is necessary, to guarantee the accuracy and stability of the experimental technique and the reproducibility of the results, a control experiment with initial conditions such as the following: 3 ppm toluene, 1.25 ppm NO, 0.05 ppm $NO_2$. Kopczynski (1972) has shown that about half of the hydrocarbon will be lost, the $NO_2$ peak will be reached in about two hours, and about 0.5 ppm of ozone will form. Tests such as these are admittedly time consuming, for they require an entire day, but they are absolutely necessary if the chamber data are to be used for mechanism validation purposes.

It is also necessary for the investigator to characterize his chamber quantitatively. Some considerations include knowledge of the rate of loss of the individual pollutants to the walls under standard operating conditions, the effect of relative humidity and mixing on the observed photochemistry, the shortcomings, inaccuracies, and imprecisions of the analytical instruments, and the rate of dilution of the reactants due to sampling. The necessary procedures must, of course, be carefully defined and meticulously planned.

## APPENDIX A. THE DETERMINATION OF $k_1$ IN AIR

In part A of this chapter we described a method for determining $k_1$ in an inert atmosphere. However, there is a great need for a general method of computing $k_1$ from the $NO_2$ concentration vs. time data collected during the photolysis of a given mixture of $NO_2$, $N_2$ and $O_2$ (such as $NO_2$ in air). This need arises for two reasons. First, it is often difficult to purge all the $O_2$ from a system of $NO_2$ and $N_2$, and thus it is of interest to know at what level of $O_2$ impurity deviations from the behavior of a pure $NO_2$-$N_2$ system begin to appear. Second, with the advent of large outdoor irradiation chambers, it will be impractical to determine $k_1$ in an $NO_2$-$N_2$ system; rather, one must be able to estimate $k_1$ from an $NO_2$-air system. We present in the appendix a general method for directly and accurately determining $k_1$ from the $NO_2$ concentration-time data gathered during the photolysis of a mixture of $NO_2$, NO, $N_2$ and $O_2$ of any initial concentration.*

The method is the following. One irradiates $NO_2$ or $NO_2$ and NO in $N_2$ and $O_2$ (e.g. dry air), noting the initial concentrations and thereafter recording the $NO_2$ concentration in the system at several times over the course of the irradiation, for example, every minute or so for a period of ten minutes. The experimental data obtained can be denoted by $NO_2^{exp}(t_i)$, $i = 1,2,\ldots,R$, where R is the number of data points. Since the reaction mechanism of a system consisting of $NO_2$, NO, $O_2$ and is known, and all the rate constants except

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* It is important to point out that the validity of this approach is subject to experimental confirmation under a range of conditions. Such verification is necessary to guarantee that the mechanism in Table 8 completely describes the chemistry of $NO_x$ in the presence of $O_2$.

$k_1$ are known (see Table 8), one can numerically integrate the differential rate equations governing the system, given any assumed value of $k_1$. Let us denote the result of this integration by $NO_2^{calc}(t)$. The objective, then, is to determine that value of $k_1$ which produces the closest match between the calculated $NO_2$ concentrations, $NO_2^{calc}(t_i)$, and the experimental concentrations, $NO_2^{exp}(t_i)$.

A useful way to quantify the stated problem is as follows: Find that value of $k_1$ which minimizes the unweighted least squares objective function

$$S = \sum_{i=1}^{R} [NO_2^{exp}(t_i) - NO_2^{calc}(t_i)]^2 \qquad (35)$$

(If we suspected that some data points were subject to more experimental error than others, we might weight the residuals so as to reflect these differences.) We thus wish simply to estimate a set of constant parameters (in this case, only one) in a system of ordinary differential equations, given a set of experimental data, a problem that has received an enormous amount of attention in the literature, particularly with regard to chemical kinetics (for example, see Bard and Lapidus , 1968) . A particularly efficient technique for carrying out the minimization of S is called quasilinearization, a procedure which essentially involves an extension of the Newton-Raphson method to systems governed by ordinary differential equations. For details of the method we refer the reader to Lee (1968) and Seinfeld (1970).

In order to estimate $k_1$ using this technique we need first to formulate the differential equations for the species in the mechanism in Table 8. A differential equation is not needed for oxygen atoms, as the concentration of this species is at steady state. Let $[NO_2] = z_1$, $[NO] = z_2$, $[O_3] = z_3$, $[NO_3] = z_4$, $[O_2] = z_5$, $[N_2O_5] = z_6$ and the desired parameter $k_1 = z_7$. Using the steady state relation,

$$[O] = z_1 z_7 / (k_2 z_5 [M] + k_4 z_1 + k_5 z_1 [M] + k_7 z_2 [M]) \qquad (36)$$

in the rate equations for $z_1$ to $z_6$, we can write the rate equations in the form

$$\frac{dz_i}{dt} = g_i(z_1, \ldots, z_7) \quad i = 1,2,\ldots,6 \qquad (37)$$

In addition, since $k_1$ is constant,

$$\frac{dz_7}{dt} = g_7 = 0 \qquad (38)$$

The $g_i$ are obtained directly from Table 8. The differential equations (37) can be integrated easily on a digital computer.

We now summarize the digital computer algorithm for estimating $k_1$ (the derivation of the algorithm may be found in Lee (1968)):

1. Make an initial guess for $k_1(z_7)$ and integrate Equations 37 from $t = 0$ to $t = t_R$. Denote this solution by $z^{(0)}(t) = [z_1^{(0)}(t),\ldots,z_7^{(0)}(t)]$ .
2. Solve the six homogeneous equations

$$\frac{d\phi_i}{dt} = \sum_{j=1}^{7} \left(\frac{\partial g_i}{\partial z_j}\right)_{\underset{\sim}{z}^{(0)}} \phi_j ; \ \phi_i \ (0) = 0$$

$$i = 1,2,\ldots,6 \tag{39}$$

from $t = 0$ to $t = t_R$ with $\phi_7 = k_1^{(0)}$, the initial guess.

3. Solve the six inhomogeneous equations

$$\frac{dp_i}{dt} = g_i^{(0)}(t) + \sum_{j=1}^{7} \left(\frac{\partial g_i}{\partial z_j}\right)_{\underset{\sim}{z}^{(0)}} (p_i - z_i^{(0)}) \tag{40}$$

$$p_i(0) = z_i(0) \ i = 1,2,\ldots 6$$

from $t = 0$ to $t = t_R$. Note that $p_7(t) = 0$.

4. Compute an improved estimate of $k_1$ from

$$k_1^{(1)} = \frac{\sum_{r=1}^{R} [NO_2^{exp}(t_r)\ \phi_1(t_r) - p_1(t_r)\ \phi_1(t_r)]}{\sum_{r=1}^{R} \phi_1^2(t_r)} \quad (41)$$

5. Generate improved values of $z_i(t)$ from

$$z_i^{(1)}(t) = k_1^{(1)}\ \phi_i(t) + p_i(t) \quad i = 1,2,\ldots,6$$

$$z_7^{(1)}(t) = k_1^{(1)} \quad (42)$$

6. Return to step 2 using $\underset{\sim}{z}^{(1)}$ in place of $\underset{\sim}{z}^{(0)}$.

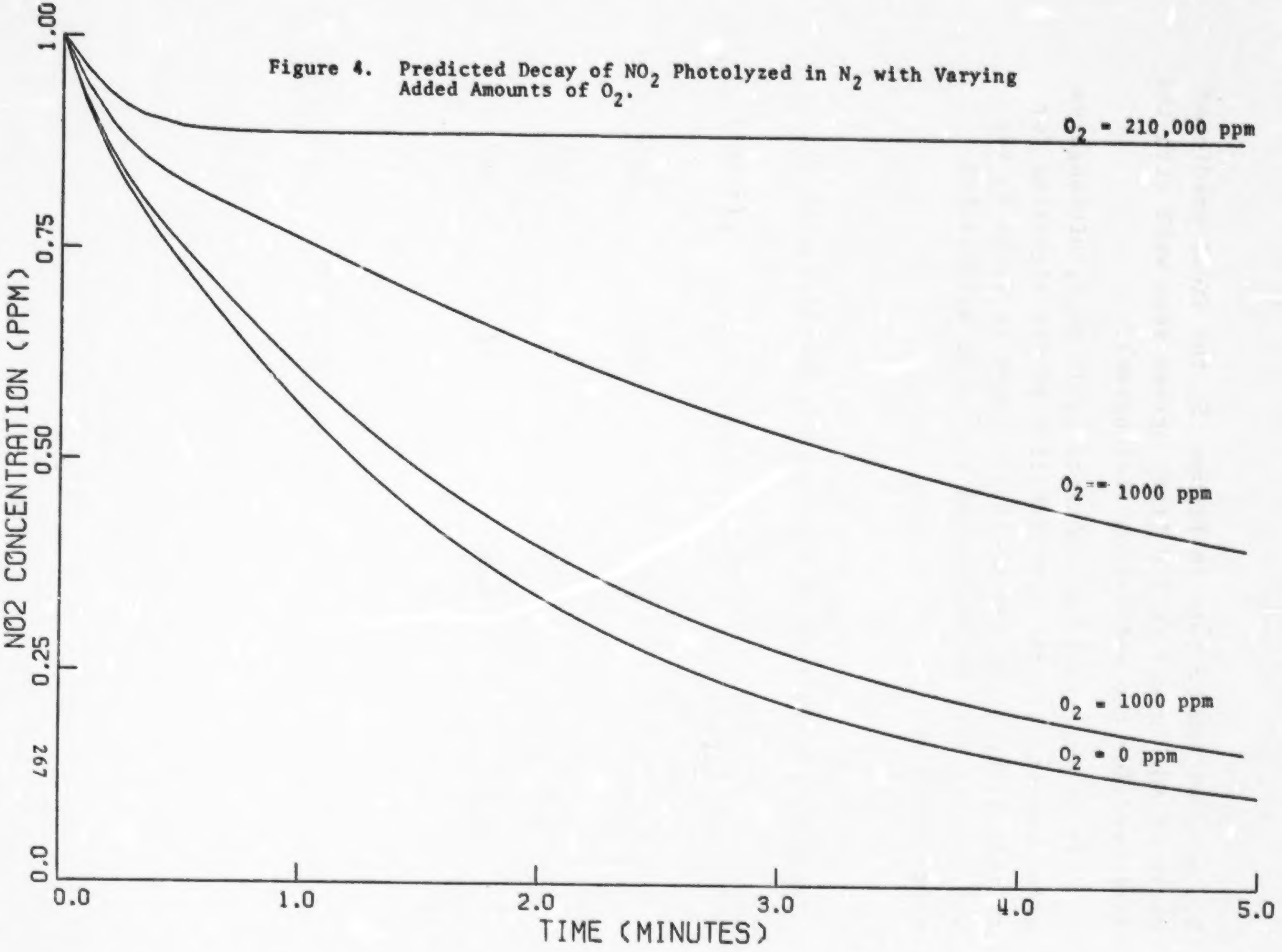
7. Continue to iterate until a subsequent estimate of $k_1$ does not change by more than some preset criterion (e.g., 0.001),

$$\frac{\left|k_1^{(\ell+1)} - k_1^{(\ell)}\right|}{k_1^{(\ell)}} < \varepsilon$$

Although we have not obtained experimental data with which to test the algorithm, we have been able to assess theoretically the effect of $O_2$ on the decay rate of $NO_2$ in sunlight. Figure 4 shows the effect of the level of $O_2$ on the $NO_2$ behavior during irradiation, based on the mechanism shown in Table 8. We note that, as the amount of oxygen present increases, the initial rapidity of disappearance of $NO_2$ increases, but the total amount of $NO_2$ lost over a fixed time of irradiation decreases. Thus, two potential measurement problems exist in such an experiment. First, small changes in $NO_2$ concentration must be detected. For example, upon irradiation of 1 ppm of $NO_2$ in air, only 10% of the initial charge is lost over a five-minute interval. Second, since the greatest change in $NO_2$ concentration occurs in the first minute, measurements must be carried out rapidly. Instrument response time is important in this regard. Both problems might be circumvented by measuring the accumulation of NO instead of the depletion of $NO_2$, since NO can be measured more accurately and quickly than $NO_2$ (e.g., by chemiluminescence). The algorithm presented requires only minor modification if NO, rather than $NO_2$, is to be measured.

We have tested the algorithm for estimating $k_1$ for the $NO_2$-$N_2$-$O_2$ system by generating $NO_2$ vs. time data for $[NO_2]_o$= 1 and 10 ppm and $k_1 = 0.4\ min^{-1}$ through numerical integration of the mechanism in Table 8. Five data points, collected over a period of 1.5 minutes, were selected as "experimental data" with which to estimate $k_1$ using the algorithm. The results of the computer experiments are summarized in Table 9. The algorithm rapidly converged to the "true" value of

Figure 4. Predicted Decay of $NO_2$ Photolyzed in $N_2$ with Varying Added Amounts of $O_2$.



$k_1$, and, as can be seen in Figure 5, the final predicted decay of $NO_2$ in air (solid line) agrees very well with the data used for the estimation (triangles).

It is important to emphasize again that, although we have demonstrated the applicability of the algorithm for estimating $k_1$ using the mechanism shown in Table 8, the validity of this mechanism has yet to be established experimentally.

Table 9. Estimation of $k_1$ from $NO_2$ Photolysis in Air

| $NO_{2\ o}$(ppm) | $k_1^{(0)}$ $(min^{-1})$ | Iterations | $k_1^{(final)}$ $(min^{-1})$ |
|---|---|---|---|
| 1.0 | 0.2 | 13 | .400 |
| 1.0 | 0.35 | 10 | .400 |
| 10.0 | 0.35 | 12 | .399 |

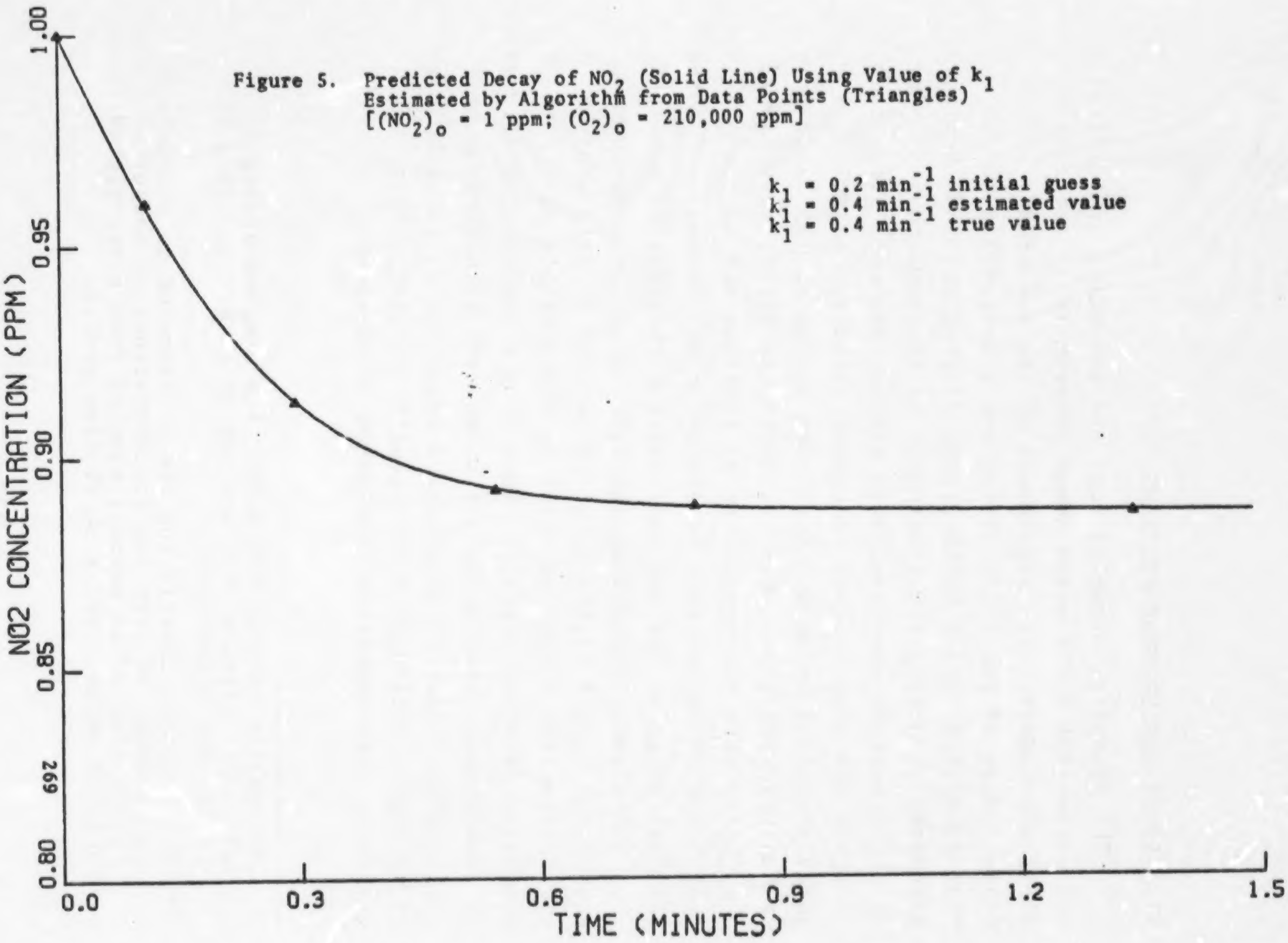


Figure 5. Predicted Decay of $NO_2$ (Solid Line) Using Value of $k_1$ Estimated by Algorithm from Data Points (Triangles) $[(NO_2)_o = 1\ \text{ppm};\ (O_2)_o = 210{,}000\ \text{ppm}]$

## VI. FIELD MEASUREMENT PROGRAMS

The planning, organization, and execution of a useful and successful field measurement program is a particularly difficult undertaking, regardless of the modestness of its scope. Many of the difficulties are attributable to the fact that there are a multiplicity of physical and chemical processes occurring simultaneously in the atmosphere. Many of the processes are complex in nature, and most are variable in space and time. Since we cannot exercise control over these processes as we do in varying degree in the laboratory, we can only passively observe, hoping to filter some signal associated with the phenomenon of interest out of the substantial level of noise* that is likely to be present. If observational programs are not undertaken with great care - that is, with clearly defined objectives, carefully conceived measurements, and highly specific methods of data analysis - the information sought may well be inaccessible due to the dominance of other signals. Most of the remaining difficulties in atmospheric observation are associated with instrument limitations - lack of accuracy or specificity, incapability of making a particular measurement**, or incapability of measuring with requisite resolution or frequency.

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* Not really "noise" but rather the complex aggregate of all other signals that are not of interest during the particular observation.

** For example, identifying the presence of an atmospheric contaminant at very low concentrations or measuring the composition of an aerosol sampled from a restricted spatial volume over a short time period.

If measurement in the atmosphere and observation of atmospheric phenomena are such difficult and potentially unrewarding undertakings, why should attempts at carrying out such programs be considered at this time? There seem to be two major reasons:

1. Certain atmospheric phenomena cannot, for one reason or another, be simulated in the laboratory. For example, we cannot yet simulate the range of atmospheric turbulence in a controlled manner, so as to establish the possible effects of transport limiting processes on observed rates of chemical reaction.
2. The existence or occurrence of certain phenomena must be identified, and this identification must be made in the atmosphere. For example, we may wish to detect $HNO_2$ in the atmosphere before we undertake laboratory studies to simulate its behavior and to assess its importance in the production of smog.

If, in the second case, we can learn enough about a phenomenon to adequately characterize it, it may then be possible to simulate the phenomenon in a controlled environment, thereby permitting more desirable conditions of observation. However, some phenomena, even if properly characterized, may be so difficult to simulate that our inability to create controlled conditions for their observation and analysis may prove to be the critical obstacle to achieving a full understanding of atmospheric processes. The coupling of turbulent transport and chemical reactions may well be such a phenomenon.

In this planning document, we are to focus primarily on those phenomena that are predominantly "chemical" in nature. However, in considering atmospheric observations one is always faced with the fact that fluid dynamical processes--advection and turbulent diffusion--are always in evidence and are often dominating in their influence on observables. It is thus quite impossible to study chemical dynamics, per se, in the atmosphere. We are, in fact, really quite limited in what we can accomplish in carrying out "chemical observations". The nature of observational programs to be proposed reflects these rather severe limitations inherent to atmospheric studies.

A number of efforts have been mounted over the last few years to assess the status of our knowledge of atmospheric chemistry and to make recommendations as to the directions that future efforts might take. In 1969, the American Chemical Society (reference cited) prepared a report that had a two-fold purpose--assessment "of the current status of the science and technology of environmental improvement" and presentation of recommendations "of measures that, if adopted, should help to accelerate the sound development and improvement of that science and technology". While the focus of the study was on chemistry and chemical engineering, the scope was broad--air, water, solid wastes, and pesticides. As a result, recommendations tended to be encompassing rather than specific. Shortly thereafter, in 1970, MIT sponsored a series of far-reaching environmental panel studies, one of which, "Man's Impact on the Global Environment: Assessment and Recommendations for Action", touched on problems in atmospheric pollution.

But, as the title implies, the study's focus was global rather than regional, its concern more with climate and longer term phenomena than mesoscale processes and short-time periodicities.

Two more recent publications, the results of studies undertaken by the TR-1 Research Committee of APCA (1971) and the Chemist-Meteorologist Workshop (1972), deal more specifically with regional air pollution problems and related areas of research and study. The TR-1 Committee conducted a survey of APCA members to determine principal areas of research need. Their report provides a very complete compilation of problems in seven principal areas--sources, sampling and analysis, control technology, atmospheric phenomena, effects, control agencies and related topics, and system definition and optimization. The Chemist-Meteorologist Workshop was composed of four panels, one of which was concerned with "Regional Studies of Atmospheric Pollution from Near-Surface Sources". The panel dealt directly with problem areas of concern--transport and dispersion, atmospheric transformations, removal processes, effects of air pollutants, sources, and aerometric measurements. They presented descriptions of past, current, and planned field studies (including RAPS), and they set forth a series of general and specific recommendations. In both of these studies, most important problem areas were identified and research needs pinpointed. However, in neither study was there an attempt made to delineate an experimental and observational program geared to carrying out recommendations made.

The most ambitious effort that has been made to date in planning a field study for enhancing knowledge in air pollution is that mounted by the Stanford Research Institute (1972). In Part II of their four-part report dealing with the proposed Regional Air Pollution Study (RAPS) to be carried out by EPA in St. Louis over the period 1973 to 1978, they present a very detailed research plan. Three research areas comprise the plan--meteorological processes, atmospheric chemistry and transformation processes, and emissions estimates. The report, in dealing with chemical phenomena, focuses on the $SO_2$ cycle, the photochemical cycle, the particulate cycle, rainfall measurements and collection, and the CO cycle. Sources, important reactions, and removal processes for each pollutant, or class of pollutants, are reviewed. Each review and discussion is followed by a series of recommended measurements and observations to be carried out for that class of pollutants. In general, the report gives recognition to known species of importance and specifies measurements that will be of value in the validation of regional airshed models. Attention is given primarily to routine measurements and monitoring, although it is recommended that a number of "special" measurement programs be carried out on a limited basis. The report is quite thorough and provides a valuable contribution to the planning of an integrated and comprehensive interdisciplinary field program.

We make no attempt to assess, codify, or critically review the SRI recommendations here. Rather, we have sought to identify specific areas of inquiry:

1. for which atmospheric observations are necessary, areas in which laboratory and/or chamber studies will not suffice
2. in which knowledge gained will be of substantial value in the development of simulation models of transport, diffusion, and chemical reaction processes in the atmosphere
3. concerned with phenomena primarily of "chemical" content, as distinguished from transport, emissions, etc. However, to the extent that transport and/or diffusion mask the chemical processes of interest, we have also given attention to these "interfering" phenomena.

Specifically, we will consider four general areas of study. These center on carrying out observations for the purpose of elucidating:

- *The coupling of transport and chemical processes in the atmosphere*. Included are observations supportive of validation of both Lagrangian and Eulerian simulation models of regional scale. Major areas of inquiry include assessment of validity of the parcel concept, quantification of the effect of turbulent diffusion on "apparent" reaction rate constants, and identification of atmospheric pollutant sinks through observation of critical ratios

($CO/NO_x$, $C_2H_2/NO_x$) as a function of location, elevation, and time. Data collection programs to be carried out in the vicinity of plumes and roadways are also considered; these data are of use in the validation and improvement of "local" simulation models.

*The nature of heterogeneous reactions affecting the distribution of atmospheric pollutant concentrations.* We consider two distinct classes of observations--those concerned with reactions involving solid or liquid materials suspended in the atmosphere (aerosols and particulates) and those involving reactions, largely biochemical, which take place at the "walls of the atmospheric reactor"; i.e., reactions with soils, vegetation, and the like. With regard to suspended materials, it is of primary interest to characterize them with respect to size and number distribution, concentration, and composition. If this can be successfully accomplished, we can then address the problem of generating aerosols in the laboratory that have physical and chemical properties similar to those of the atmospheric aerosol. If such aerosols can indeed be generated in the laboratory, investigation of this class of heterogeneous atmospheric reactions can "move indoors" and be carried out under controlled conditions.

- *The effect of radiation on important photolysis reactions that occur in the atmosphere.* Reactions of primary concern include the photolytic decomposition of $NO_2$ and $HNO_2$. Of interest is observation of variations in intensity with location (including elevation) and time in an urban area to gain an understanding of the influence of water, aerosol, and particulates on attenuation of the incoming direct and scattered spectral distribution.
- *The chemical composition of the atmosphere.* The focus here is the identification and measurement of intermediates and products occurring at low concentrations. Included are PAN and other peroxynitrates, nitrogen compounds ($N_2O_5$, $HNO_3$, $N_2O_3$, $HNO_2$), aldehydes, organic acids, and peroxides. Also of interest, but extremely difficult to measure, are the multiplicity of free radical species present in the atmosphere.

A fifth area of inquiry that merits attention is the development and testing of instruments that will enable investigators to carry out measurements in situ and at concentrations one to two orders of magnitude less than can currently be accomplished. Such instrumentation is needed if measurement programs in the four areas outlined are to be carried out successfully. However, we will not attempt here to suggest research programs in expanding instrument capabilities and developing new tools; delineation of such programs is beyond the scope of this effort. Rather, we mention it to indicate that pursuits in all areas of atmospheric observation are critically dependent on the range, accuracy, and selectivity of instruments, that the ambitiousness of the effort mounted must, in the end, be determined by the quality of measurements that can be carried out, and, as a result, that instrument development merits as great a degree of attention as the field measurement effort itself.

In the sections that follow, we examine each of the four areas of inquiry in greater detail. In discussing them we address the following questions:

- *What is the specific objective envisioned?*
- *What type or types of measurements (or observations) are needed to meet these objectives?*
- *What method or methods will be applied in the analysis of the data collected?*
- *What is the nature of the expected result (utility, accuracy, applicability, etc)?*

## A. Effects of Transport and Diffusion on Species Distribution and Chemical Rate Processes

As we have emphasized, atmospheric phenomena are characterized by strong coupling between physical (transport and turbulent diffusion) and chemical rate processes. The nature of this coupling has been examined rather fully in Chapter III. Chapter V is devoted specifically to topics involving the study of chemical rate processes *in the absence of transport limitations*. In this section we address the extremely difficult problem of carrying out investigations of atmospheric chemical processes *in the presence of transport and diffusion limiting rate processes*. But first we review that body of previous work which has served to define the role of turbulent transport processes in determining chemical rates.

The importance of the effect of turbulent fluctuations and degree of mixing on chemical reactions has long been recognized. In his classical treatise on the interactions of dynamics and chemical kinetics of reacting systems, Frank-Kamenetskii (1947) discussed a particular case of turbulent combustion in which the fuel is fragmented into small discrete parcels distributed in the airstream. The rate of combustion was found to be controlled not by the chemical reaction rate but by the turbulent mixing of fuel and air. The implication is that, for sufficiently fast reactions, the reaction rate is governed not only by the magnitude of the rate constants but also by the rapidity with which turbulence can bring the reacting species into contact. In a similar context, von Kàrmàn (1953) emphasized the desirability of developing statistical theories for reacting flows. More recently, Corrsin (1961, 1964) considered the interaction of first- and second-order isothermal reactions and stationary, isotropic turbulence and found that the spectrum of turbulent concentrations is significantly affected by the existence of chemical reactions.

O'Brien (1968a, 1971, 1972) has also considered the interaction of turbulence and chemical reactions. For very rapid reactions, he found that the random concentration field consists of two distinct phases: a first stage in which the reactions proceed in tiny fluid fragments before turbulent mixing begins and a second stage in which the fluid fragments, having reacted to completion individually, are folded together and mixed by the turbulence. The most significant result of this analysis is that, even if at the beginning of the first stage the mixture is fairly uniform, at the end of that stage there may exist strong concentration inequalities as a result of the very rapid reaction in localized fluid particles.

As mentioned in Chapter III, Donaldson and Hilst (1972) have shown in a recently completed study that chemical reactions may be slowed considerably by concentration fluctuations. The magnitude of this effect is determined by the intensity of the fluctuations. In the limiting case of no molecular diffusion, no apparent chemical reaction occurs at the end of the first stage of the reaction even though considerable amounts of both reactants are still present. However, there is some doubt as to whether the results of this simple model apply in a real situation, as the validity of the assumptions imposed come into question. The importance of two factors, in particular, must be examined--the effect of higher order correlations and the counteracting effect of both turbulent and molecular diffusion.

Experimental tests have confirmed various aspects of the theoretical results that we have discussed. For very fast reactions in a turbulent field, the asymptotic reaction rate is governed by the rate of turbulent mixing, and not by the absolute chemical rate of the homogeneous reaction. However, it must still be demonstrated by measurements that the amplitudes and intermittencies of the concentration fluctuations in the atmosphere are such that the turbulence-chemistry interaction cannot be neglected (Vassilatos and Toor (1965) and Keeler, et al. (1965)). Previous experiments of this kind have been plagued by poor accuracy or slow response of conventional instruments. However, a breakthrough in measuring ozone and nitric oxide has been recently reported (Stedman et al. (1972)). A chemiluminescent technique with an accuracy in the ppb range and a time response of less than 10 seconds was used to monitor the ambient air downwind of roadways in Detroit, New York, and Boston. Stedman et al. reported that rapid fluctuations of nitric oxide and ozone were observed and, more significantly, that the measured NO and $O_3$ concentration/time profiles were found to be 180° out of phase with each other.

Since one would expect that emissions, immediately after their release from sources, should be uncorrelated or positively correlated, it is our opinion that the strongly negatively correlated concentrations that were observed provide substantive evidence that the interaction of chemistry and turbulence does take place in the atmosphere. Eschenroeder et al. (1972) have analyzed some of these data and found that the correlation coefficient is as high as -0.742. We have further studied these same data and found that

$$\frac{\overline{c_{NO}^{2}}}{\overline{c_{NO}^{2}}} = 0.0978 \text{ and } \frac{\overline{c_{O_3}'^{2}}}{\overline{c_{O_3}^{2}}} = 0.011$$

Based on these results, the theory developed by Donaldson and Hilst would imply that the apparent $O_3$-NO reaction rate will decrease and approach zero asymptotically even when about 20% of the original reactants remain. These estimates are only approximate because, as we have mentioned earlier, the effects of higher order correlations and diffusion have not been considered in the model. In particular, diffusion tends to smooth the concentration gradients and oppose the fluctuations created by the interactions between chemistry and turbulence.

In conclusion, both the theoretical and experimental studies carried out thus far clearly indicate that the effect of coupling between chemical reactions and turbulent fluctuations is important in determining the reaction rates of photochemical reactions in the atmosphere.

In the introduction to this chapter we have alluded to the difficulties inherent to atmospheric observational studies. It is clear that laboratory simulation of atmospheric phenomena is preferable when feasible, as we can exercise control over the experiment. However, it is quite difficult to simulate certain aspects of atmospheric processes, particularly those involving the interaction of turbulence and chemistry. Also, we are unable in many instances to suppress or eliminate those phenomena that occur in the laboratory but not in the atmosphere. More specifically, chamber studies are characterized by a high degree of mixedness, restricted size of the experimental system, artificial light sources, and the absence of aerosol or lack of controllability of aerosol properties. In addition, the turbulence level in an unstirred smog chamber will typically be low compared with levels existing in the free atmosphere. Thus, in extrapolating the results of such studies for application in the analysis of atmospheric observations, we find that we are incapable of properly dealing with spatial nonuniformities, turbulent fluctuations, and the effects of aerosols. Furthermore, we do not yet know how to assess and thus properly compensate for certain "chamber effects", such as reaction at the walls. Finally, the degree to which the atmospheric spectral distribution of radiation has been properly simulated in the chamber is uncertain. Thus, despite the difficulties that inhere to an observational program, we must still undertake such programs to obtain information fundamental to gaining an understanding of the effect of turbulence on chemical rate processes.

Having discussed the importance of the coupling of chemistry and transport and the need for an observational program, we must now consider how best to structure such a program. It is important to state at the outset that any division of effort will, of necessity, be somewhat arbitrary. However, we herein present our thoughts on the matter. One useful means for segmenting an observational program focuses on validation of models, in the hope that discrepancies between observation and prediction will indicate in what respects and to what extent our knowledge is deficient.

Analysis of the data collected will perhaps suggest further studies to be carried out in the laboratory or in the smog chamber that will be useful in clarifying dilemmas. Another method of grouping involves the identification of specific gaps in our knowledge and the design of an experimental program with these in mind. As a matter of convenience, we have elected to segment this discussion according to the modeling framework, as follows:

- Regional Scale Studies
    - Lagrangian Program
    - Eulerian Program

- Local Scale Studies
    - Plumes
    - Roadways

We find this division useful because, by examining the model, it is an easy matter to identify the questions that might be raised, the quantities that must be measured, the effects of uncertainty in the various parameters of interest, and the like. The model is in effect a tool useful in organizing thought. However, within each section we will also address issues that do not arise solely because of modeling considerations; each will be included in the section that seems most appropriate. For example, material balances will be discussed as a part of regional fixed grid studies, whereas the investigation of "apparent" kinetics will be a part of regional Lagrangian studies.

### 1. Regional Scale Studies

Topics of discussion in this subsection are restricted to measurements and observations to be made in a program of regional scale--of the order of 10 to 50 miles. Not all topics, however, must be included in a program of this scale. Some observations should also be made (and perhaps are better placed) in programs of more limited spatial extent (for example, the study of the effects of turbulent fluctuations on chemistry); others are included as a matter of convenience in classification. However, all will be of value in providing information useful in the modeling and analysis of phenomena that are of interest on a regional scale.

#### a. A Lagrangian Program

In many ways the parcel concept is the natural framework for studying atmospheric chemistry. As a parcel of air is advected through an urban area, it accepts pollutants emitted both at the ground and aloft. Chemical reactions take place within the parcel, and secondary pollutants are formed. However, it is generally assumed that the parcel does not exchange material with its surroundings (except for direct emissions), nor does it respond to vertical movements of air. We thus may view the parcel quite simply as a horizontally transported chemical reactor with variable rates of reactant input and removal.

Unfortunately, serious questions arise as to the validity of the parcel concept, questions which we have discussed rather fully in Chapter III. The major issues center on the following arguments:

- At low wind speeds, turbulent diffusion contributes heavily to net transport. "Parcels" tend to "disintegrate" under these conditions and cannot be clearly defined.
- Under conditions of intense incoming radiation and thus strong ground heating, or when transport takes place over terrain of rapidly varying elevation, vertical movements can be important. These tend to destroy "parcels".
- Wind speed and direction can vary with height. Under such conditions, parcels are subjected to shear, are distorted and fragmented, and are ultimately destroyed,

The first two conditions described tend to be prevalent on "high pollution" days in the Los Angeles area, days for which the use of such a model would be of particular interest.

One can view the question of parcel integrity in another way. Consider at one extreme a parcel having small dimensions--say ten meters in diameter. A parcel of this size is subject to the effects of shear, of turbulence, and of exchange with its surroundings (having a relatively large surface-to-volume ratio) during its traverse across an urban area. It would be surprising if a parcel of this size would remain an identifiable entity over, for example, a 1,000 meter traverse. In contrast, consider a parcel of 2,000 meter diameter. This parcel would be virtually unaffected by local fluctuations and variations and would exchange little mass with its surroundings. But within the parcel there are likely to be large variations in concentration at any one time. A great deal of chemical detail is thus unresolved. A parcel of interest, then, lies somewhere between these two extremes in size--between 200 and 1000 meters in diameter. To what extent does a parcel of this size maintain its integrity over time periods of interest on an urban scale--periods of two to eight hours in duration? To what extent do turbulence, buoyancy, and shear alter the size, shape, and structure of the "parcel"? How is the degree of mixedness affected by these processes? To what extent do "high-concentration" packets of air, heated at the ground, rise and penetrate the parcel -- thereby introducing "new air" and fresh pollutants?

Two observational programs having the parcel concept as their core are now in the planning stages. One, being planned at Stanford Research Institute, involves monitoring parcel movements along the centerline of San Francisco Bay, following the parcel southeastward to the San Jose area from the point at which it leaves land at the eastern side of San Francisco. Air quality and meteorological measurements will be made from a houseboat that will follow a tetroon along its trajectory. A major consideration in mounting this study is that it has been observed that air movements consistently follow the Bay centerline toward the southeast during periods of high oxidant formation (Robbins and Cavanagh (1972)). As the parcel passes over water during the period of observation, the only pollutant sources along its path are the two bridges crossing the central and southern portions of the Bay. Thus, the parcel approximates a moving, unbounded chemical reactor with virtually no sources and only minor sinks.

The second program, currently being planned by W. A. Perkins of Metronics Associates, consists of a very comprehensive monitoring study in the Los Angeles Basin. Parcels will be identified and tracked through use of tetroons and radar. Helicopters will measure air quality in the vicinity of the tetroon, and both laterally and vertically. Aircraft will be employed in measuring winds aloft. A mobile van will follow the tetroon, obtaining air quality data while in motion. Tracer materials (either fluorescent particles or $SF_6$) will be released with the tetroon and will be collected both at the ground and aloft. Multiple tetroon launches will be made to assess the validity of the parcel concept.

Both programs are currently being planned, and, as a result, no formal documents are yet available which describe the projects. However, pertinent reports of a preliminary nature are available--Robbins and Cavanagh (1972) and Perkins (1972). We refer the reader to these to gain a better understanding of the planned program; we will not attempt to describe them here. Rather, the reader should assume that the commonly made and more obvious measurements will be carried out. We will consider here only measurements or observations of a more specific nature--either those useful in exploring the effects of transport and diffusion on chemical rate processes or those that are a logical adjunct to a Lagrangian field study. The entire data base, of course, will be used in the validation of Lagrangian models.

The major issues with which we will concern ourselves here are:

- *Investigation of the validity of the parcel concept.* Over what range of conditions--wind speed, wind shear, level of turbulence, nature of terrain, intensity of radiation (surface adsorption and convective heating)--does a parcel maintain its integrity for time periods commonly of interest? Over what spatial scale? To what extent do turbulent processes induce lateral and vertical diffusion?
- *Characterization of the degree of mixedness of a parcel.* To the extent that reactants in a parcel are not intimately mixed, their access to each other is limited. Apparent reaction rates under these conditions can be substantially less than absolute reaction rates.
- *Characterization of turbulence* to aid in determining the effects of these processes on observed reaction rates, as well as on the chemical mechanism assumed. High levels of turbulence will encourage mixing and lessen the effect of transport limitations on apparent kinetics.

The measurements that we recommend be carried out are as follows:

- *Integrity of parcel*--multiple, simultaneous tetroon launches to assess magnitude of diffusion within, and in the vicinity of, a parcel; collection aloft of tracer released at surface at time of tetroon launch; variations in wind speed and direction with height; concentration of CO, NO, $NO_2$, $O_3$, and possibly hydrocarbons as a function of distance, both horizontally and vertically, in the vicinity of the tetroon. These measurements have already been recommended by W. A. Perkins (1972) for the proposed Los Angeles study and will very likely be incorporated into it.

*Mixedness*--high frequency measurements of pollutant concentrations aloft (NO, $NO_2$, $O_3$, other) as a function of time (measurement intervals of the order of $10^{-2}$ to $10^{-1}$ seconds) to permit determination of the correlation in fluctuations between pairs of reacting pollutants; measurement of CO and $C_2H_2$ concentrations in the vicinity of the parcel to aid in estimating the rate at which material is introduced to or lost from the parcel.

*Turbulence intensity*--intensity of turbulent fluctuations in the vicinity of the tetroon, employing an instrument such as the MRI turbulence meter (UITS 1120).

Analytical studies of three types are needed to treat the data collected. The first type involves direct data reduction, correlation, and analysis, employing appropriate statistical techniques, in order to identify and quantify the effects under investigation. The second entails theoretical studies, the aim of which is to establish cause-effect relationships based on phenomenological analyses. Finally, we wish to evolve methods for incorporating into urban airshed models the observed effects of transport-limiting processes on reaction rates.*

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* Specifically, we have in mind here the need for establishing relationships of the following type:

$$k_{effective} = f(k_{absolute}, \underline{K}, \overline{c'^2_i}, \overline{c'_i c'_j}, \text{other parameters})$$

where $k_{effective}$ = pseudo reaction rate constant for the atmospheric reaction of interest

$k_{absolute}$ = absolute rate constant for the homogeneous reaction, as measured in the laboratory

$\underline{K}$ = turbulent diffusivity

Such expressions have been derived for simple heterogeneous systems, an example being a first-order reaction at a surface. If the reactant species diffuses through a boundary layer of thickness $x$, then

$$\frac{1}{k_{effective}} = \frac{x}{\underline{K}} + \frac{1}{k_{absolute}}$$

Note that, when $\underline{K}$ is large, $k_{effective} \simeq k_{absolute}$, and the dynamics are reaction rate-limited. When $\underline{K}$ is small, the dynamics are diffusion-limited.

Each category of analysis merits attention as an area worthy of immediate support if the suggested observational program is to be carried out. Moreover, methods of data reduction and analysis should be carefully defined *prior to finalization of the plans for the observational program,* so that *needed* measurements will be made, so that measurements have the resolution, specificity, and accuracy required, and so that they are carried out with sufficient frequency. Specifically, as a part of planning the observational program, the following questions must be answered:

1. Exactly which parameters should be measured?
2. What specifications (or constraints) should be placed on each type of measurement (i.e., in terms of specificity, accuracy, frequency, etc.]?
3. What instrument (or type of instrument) should be used for the measurement?

In concluding this discussion, we will comment briefly on the planning aspects, without attempting to deal with questions of post-observational analysis.

We have suggested in our recommendations what parameters might be measured. However, we have not been sufficiently specific in some areas. For example, Donaldson and Hilst have found that, for a reaction involving only two species and under special conditions, the assessment of inhomogeneities in concentration of the participating species and their cross-correlation, as measured by $\overline{c'^2_\alpha}$, $\overline{c'^2_\beta}$, $\overline{c'_\alpha c'_\beta}$, respectively, are of primary importance in estimating the magnitude of departures in concentration from those expected in a homogeneous system. However, it may well be that higher order fluctuations are also determining factors, in which case the fluctuations of a third species should perhaps also be followed. Furthermore, to the extent that molecular diffusion influences the intensity of fluctuations, key parameters that reflect the magnitudes of these coefficients should also be monitored. Theoretical studies, however, do not constitute the only means for identifying these parameters; identification may be achieved by adopting novel investigatory approaches. For example, Eschenroeder et al. (1972) have proposed that deviations from quasi-equilibrium (for the reactant system, NO, $NO_2$, $O_3$) can be used to indicate the magnitude of the effect of turbulence on chemistry. Despite the fact that quasi-equilibrium may never be realized, even in a perfectly homogeneous atmosphere, because of the effects of competing reactions, this type of analysis, nevertheless, deserves further investigation.

With regard to specifications that might be placed on a particular type of measurement, we refer primarily to questions of accuracy, specificity, frequency and/or duration of measurement, etc. For example, the frequency with which concentrations are measured for the purpose of correlational analysis to assess the degree of mixedness must be determined prior to the beginning of the observational program. If measurements are made, say, at 1-second intervals, but theoretical analysis suggests that measurements of 100 $\sec^{-1}$ frequency or greater are needed to support meaningful analysis of the concentrations fluctuations of two reacting species, then observations taken at one-second intervals will be of little use. To present this in more precise terms, consider the cross correlations $\overline{c'_\alpha c'_\beta}$, where

$$\overline{c'_\alpha c'_\beta} = \frac{1}{T}\left[\int_0^T c'_\alpha c'_\beta dt\right] - \int_0^\infty \phi_{\alpha'\beta'}(\nu)d\nu$$

where $\phi$ is the co-spectrum and $\nu$ is the frequency. Although concentration fluctuations of all frequencies may appear, contributions from only a finite range are dominant in computing this double correlation. It is therefore important to decide in advance how to choose the upper and lower cut-off frequencies, $\nu_U$ and $\nu_L$, respectively, so that we may adequately approximate the above integral by

$$c'_\alpha c'_\beta \approx \int_{\nu_L}^{\nu_U} \phi_{\alpha'\beta'}(\nu)d\nu = \int_{\ln\nu_L}^{\ln\nu_U} \nu\phi_{\alpha'\beta'}(\nu)d\nu$$

The choice will, of course, depend upon the particular situation, but, in any case, will be the major determinant in properly specifying the frequency of observation, and thus the resolution of the monitoring apparatus. In general, then, questions concerning accuracy, specificity, and frequency of observation must be raised, carefully stated, and answered prior to planning the actual measurements if truly useful data are to be collected.

The need for judicious selection of instrumentation seems self-evident. Data collected will be of little or no use if they do not satisfy the requirements discussed above. For example, experimental evidence of the interaction between turbulence and chemical kinetics can be obtained only if a highly stable, highly sensitive (capable of measuring in the parts per billion range), and short time response ( 1 sec) measuring device, such as the chemiluminescence method, is available. Clearly, careful studies must be carried out to determine the capabilities of the existing instruments.

One final comment seems appropriate regarding planning of the measurement program and analysis of the results. Angell and his co-workers have for several years carried out observational programs in the lower troposphere involving the use of tetroons and have established a substantial level of expertise (Pack et al. 1970; Angell et al. 1971a,b,c,d; 1972a, b). Their studies have provided a rich collection of data involving such diverse phenomena as horizontal and vertical movements of air parcels, rates of dispersion, helical circulations, and urban heat island effects. Of particular interest is the study by Angell et al. (1971b) involving the nearly simultaneous release of tetroons, thereby providing a basis for estimating turbulent diffusivities. Angell et al. (1972b) have also carried out a comprehensive program of tetroon tracking in Los Angeles. In that program they found that, on occasion, significant variations in horizontal wind direction with elevation occur in the area. Thus, given the expertise and experience of this group, we strongly recommend that they be asked to participate in the planning of atmospheric experiments of the type we are suggesting here.

In summary, a Lagrangian regional study will provide the following:

- Means for assessing the validity of the parcel concept--if valid, its range of validity, spatially and temporally.
- Data useful in validating "moving parcel" models.
- Information useful in assessing the degree of mixedness aloft of major reactive and unreactive pollutants.
- Data useful in attempting to develop a means for incorporating diffusion-limiting effects in the kinetics portion of airshed simulation models.

### b. An Eulerian Program

While the Eulerian, or fixed coordinate, framework is a natural coordinate system for characterizing meteorology and emissions, it is in some ways a less desirable reference system than the Lagrangian for investigating questions pertaining primarily to chemistry. For this reason, we have included in the preceding discussion of observations to be carried out in the Lagrangian reference system a number of questions in critical need of study However, there are several classes of observations that would be of considerable value in elucidating chemistry insofar as kinetic mechanisms are an integral part of an airshed model. These measurements, in all cases, should be carried out so as to establish variations in the quantity measured as a function of location and time--hence, their inclusion in this section.

In general, on the basis of what has been said thus far, one might include in this discussion observation of any variable that could be of use in modeling. In an integrated and coordinated observational program, however, many measurements are commonly made, and on a routine basis. Ground level concentrations of CO, NO, $NO_2$, oxidants and wind speed and direction are examples. We will thus discuss only those measurements that are not routinely carried out, and that are in fact rarely made. In selecting these classes of observations or measurements, we have the following objectives in mind:

- Acquisition of pollutant concentration data aloft; also improved characterization of *nighttime* pollutant concentration distributions aloft. The former objective is based on the utility of such data in model verification, an exercise which has been restricted to date to evaluations at ground level. Nighttime observations are of value in establishing initial conditions and boundary conditions in models. Knowledge of variations in ozone levels aloft in the absence of radiation may shed some light on the atmospheric chemistry of this species. We may also be able to gain insight as to why multiple layers of high concentration material form aloft. (While the formation of multiple inversion layers is, of course, heavily dependent on transport considerations, the chemistry of such layers may be of considerable interest.) Finally, our knowledge and understanding of variations in concentrations aloft is poor; such information is badly needed.
- Establishment of a data base sufficient to permit a mass balance to be made for nitrogen and sulfur.

- Determination of variations in reactivity of the atmospheric hydrocarbon mixture with location and time.

Each objective, if satisfied, would improve our ability to model the atmosphere. Improved models would make more meaningful the results of sensitivity studies. These results, in turn, will better illuminate areas in which acquisition of knowledge is vital.

There are six categories of observations which we recommend be carried out to satisfy the stated objectives and which are not commonly made.* They are:

- Vertical soundings of concentration. Included are measurements of some or all of the following--CO, NO, $NO_2$, $O_3$, non-methane hydrocarbon (NMHC), $SO_2$--from the ground to 200 to 500 feet above the base of the elevated inversion. (We assume here that measurements of this kind will be made during a high pollution period, and that in such circumstances an elevated inversion will be present.) Measurements are to be made two or three times during the day (or more frequently if warranted) above two to four strategically selected ground locations in an urban area.

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* While we do not include a discussion of purely meteorological measurements, even though they may be of importance, we do wish to mention one "non-routine" class of observations--the monitoring of winds aloft. Usually, only surface wind data are available; for a comprehensive study such as we are discussing, measurement of the elevated wind field is also needed.

- Mapping of concentrations aloft at night. Measurement of some or all of the following--CO, NO, $NO_2$, $O_3$, $SO_2$--as a function of location (i.e., the x-y coordinate position) and height. Measurements to be carried out from one to three times daily during the dark hours.
- Temperature soundings, more frequently than is common. We suggest at least three soundings during the day and two or three at night, perhaps at four-hour intervals. (We note, however, that, if temperature is found to have a significant effect on the overall rate of chemical transformations in the atmosphere, then the suggested frequency of measurement will very likely be inadequate.) In an area over which the height of the inversion base varies only slightly with location at a given time, a sounding at one location will suffice. In an area such as Los Angeles, over which there is considerable spatial variation in the height of the inversion base, soundings at a number of locations are recommended. (For Los Angeles, we suggest five to six sites.)

- Measurement of the distribution of individual hydrocarbon and oxygenated hydrocarbon species as a function of location and time. This suggests gas chromatographic measurements at a number of locations spread throughout the urban area. While measurement in the vertical would be highly desirable, it is not feasible at this time. However, if the aging of bag samples can be shown to have a negligible effect on the determination of hydrocarbon distribution, delayed analysis, at ground stations, of samples collected aloft is quite acceptable.

- Execution of a "sink" inventory. This involves estimation of the available sink surface, both for aerosols and ground sinks. We discuss this more fully in Section B, *Heterogeneous Reaction Studies*.

- Measurement of the variations in radiation intensity as a function of ground location, elevation, and time. We wish here to establish a relationship between aerosol concentration (and other aerosol characteristics), cloud cover, and intensity. We discuss this topic in Section C, *Spatial and Temporal Variations in Solar Radiation*.

Because of the very comprehensive nature of this program, the measurements will involve careful planning and substantial costs. They also should be coordinated so that a full set of measurements is acquired for specific periods of observation. We thus do not view this program as being routinely, or even frequently, undertaken. Rather, we expect that, in a study such as RAPS, such observations would be made on perhaps a half dozen to a dozen occasions, with at least two or three of the days being consecutive. Clearly, it is preferred that "measurement days" be days of high pollution levels.

Analysis of data will, of course, involve the use of Eulerian airshed simulation models. In fact, the measurements suggested are, to a large extent, those that are presently needed, but unavailable, for validation purposes. However, these data, along with more routinely collected data, will also permit:

> An attempt to establish a mass balance for nitrogen and sulfur. If measurements of vertical variation of wind velocity with height are made and the concentrations of appropriate pollutants are monitored at the boundaries, incoming and outgoing mass fluxes can be estimated. With chemical reactions included in the model and an appropriate emissions inventory available, net loss to sinks can be estimated. This estimate can be compared with an independent estimate of losses to sinks, as discussed in Section B.

Calculation of ratios of reactive species to inert (or nearly inert) species as a function of location and time. Examples: $NO_x/CO$, $NO_x/C_2H_2$ (if acetylene is monitored), olefins/paraffins, $\frac{\text{olefins + aromatics}}{\text{paraffins}}$. Such "tracer" data may provide a basis for estimating rates of appearance and disappearance of reactive species. They may also be of value in estimating rates of loss to aerosols, particularly if gaseous chemistry can be clearly established.

Estimation of the extent to which equilibrium between NO, $NO_2$, and $O_3$ is approached. Equilibrium is unlikely to be established near the ground due to sources, but it may be achieved rapidly aloft. With chemiluminescent analyses, averaging times will be sufficiently short to make such computations meaningful.

Computations and analyses involving sinks and radiation will be discussed in subsequent sections.

## 2. Local Scale Studies

We have thus far given attention to observational needs that are to be met as part of a regional or urban scale monitoring program, with the focus on enhancement of knowledge in atmospheric chemistry. A similar need exists at the local scale, a need for observational studies to elucidate the nature of chemical reaction processes that occur in plumes and in the vicinity of roadways.

a. Plumes

Transport and dispersion of pollutants emitted from stacks has been a subject of investigation for many years. However, chemical reactions that take place within plumes have received relatively little attention. Nitrogen oxides and sulfur oxides are the reactive species of greatest interest in plumes, due to the high rate of emissions of these pollutants from fixed sources. The need for study of their reactions in plumes rests, not on the fact that reactions of the species have not been heavily investigated, but on the knowledge that the conditions existing in a plume (e.g., temperature, humidity, concentration):

1. May be quite different than the conditions under which reactions of $SO_2$ and $NO_x$ are carried out in the laboratory, and
2. Are often inaccurately known, if at all

Combustion products normally leave a furnace chamber at 1500-2000°F, whereupon they enter a vertical stack. As the primary function of the stack is to ensure that the product stream is dispersed well aloft in the atmosphere, safely away from people and their structures, stacks are designed to impart maximum buoyancy and high-exit velocity to the plume. Stacks are thus well insulated, thereby maintaining the vented stream at high temperature until its exit. Cooling of the stream then occurs rapidly due to the entrainment of air as the plume rises, loses buoyancy, and comes under the influence of the prevailing winds. The exiting stream, then, consisting primarily of nitrogen, $CO_2$, water, carbon monoxide, and other combustion products, and carrying $NO_x$ and $SO_2$ at temperatures of the order of 400 to 800°F as it leaves the stack, enters the atmosphere at conditions far different than ambient.

The high temperature of the plume will, of course, considerably influence rates of reaction. High temperatures also suggest the possibility of thermal reactions occurring at significant rates that are unimportant at ambient temperature. Moreover, high concentrations may favor reactions not ordinarily of interest, such as $2NO + O_2 \rightarrow 2NO_2$. The high water content of a plume suggests that rapid adsorption and dissolution of $NO_2$ takes place upon condensation of the vapor. Should conditions in the plume favor conversion of $SO_2$ to $SO_3$, sulfate-containing aerosol will immediately be formed. Finally, the high NO content of the plume implies that ozone concentrations will be low in its vicinity, due to the reaction of NO and $O_3$. The importance of these reactions and others in determining the composition of plume as it assumes ambient flow conditions is largely unknown. We thus recommend that a measurement program be undertaken to provide the data needed to investigate these questions.

A suitable measurement program would consist of monitoring stack conditions--temperature, flow rate, and composition of the exit stream--and making traverses of the plume at two to four downwind positions to measure the cross-sectional concentration distribution of NO, $NO_2$, $SO_2$, CO, ozone, and aerosol (if possible). We also suggest measuring temperature and water concentrations at each transection location. Finally, ambient temperature and pollutant concentrations, along with local meteorological parameters, should be monitored continuously in the vicinity of the plume, as should radiation intensity. The development of suitable models of reactive plumes, in conjunction with the analysis of such data, will provide valuable insight into the transformation processes that occur within these important sources of atmospheric pollutants, and we will finally gain some knowledge as to the contribution of fixed sources to air pollution on the regional scale.

### b. Roadways

While automobiles emit "plumes" at high temperatures that contain combustion products such as $H_2O$, $CO_2$, CO, $NO_x$, and partially burned hydrocarbons, our interest in studying atmospheric chemistry in the vicinity of these emissions sources stems from considerations quite different than those which are supportive of studying the chemistry of plumes emitted from large fixed sources. The exhaust stream that is emitted from the vehicle cools very rapidly, ruling out an interest in high temperature reactions It also mixes with its surroundings very rapidly *under most conditions*, due to the stirring induced by the movement of the vehicles. The conditions of interest, then, are local high concentrations of NO, $NO_2$, hydrocarbons, and CO at ambient, or near ambient, temperatures.

Of primary importance is our obtaining an understanding of the influence that the enhanced production of $NO_2$ through the $NO\text{-}O_3$ reaction has on photochemical kinetics at the local scale. Because of the steady input of $NO_x$ in the immediate vicinity of a heavily used roadway, the equilibrium between $O_3$, NO, and $NO_2$ that may exist aloft due to the reactions

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

does not hold near such sources. Ozone levels are very low, whereas $NO_x$ and hydrocarbon concentrations are elevated. It would thus be of considerable value to determine if chemical mechanisms are capable of describing the concentration behavior of these species on the local level, and to better assess how to include the observed pollutant mix as input, via an emissions inventory, in models of regional scale.

We envision an appropriate measurement program to include the simultaneous monitoring of pollutant concentrations upwind, alongside, and downwind of a major artery. NO, $NO_2$, $O_3$, NMHC, $H_2O$, and CO should be measured, along with temperatures and radiation intensity. Local meteorological conditions, including level of turbulent fluctuations, and vehicular flow rates should also be monitored throughout the period of observation. Such data will provide a basis for validating "reactive roadway models" and thus for studying the kinetics of reactions at high $NO_x$ and HC concentrations.

One final note is appropriate. In a monitoring program to be carried out in the vicinity of roadways, it would be of considerable value to collect data useful in assessing the effects of turbulent fluctuations and lack of mixedness on reaction rates. We thus recommend the use of apparatus for measuring NO, $NO_2$, and $O_3$ concentrations that are capable of high frequency determination of concentrations.

## B. Heterogeneous Reaction Studies

While the reactions of gaseous species have been thoroughly studied in the investigation of transformations of atmospheric pollutants, gas-liquid and gas-solid interactions also constitute important transformation mechanisms. Largely, these involve adsorption of pollutant species on and often diffusion into liquid droplets, suspended solid particles, and solid surfaces, whereupon reactions may take place. However, whether or not chemical reactions occur, aerosols (suspended liquids and solid particles) and surface materials do constitute sinks for pollutants. In previous chapters we have discussed the role of each in pollutant removal from the atmosphere. In particular, we refer the reader to Chapter IV for a discussion of laboratory studies of aerosol formation and to Chapter V for a discussion of the role of smog chambers in investigating natural scavenging processes. In this chapter we explore the types of atmospheric observations that might be of value in enhancing our knowledge of contaminant removal mechanisms.

### 1. Aerosols

Apparently, the first large-scale program aimed at understanding the behavior and properties of photochemical aerosols was the 1969 Pasadena Smog Experiment. During the experimental period of about three weeks (August and September 1969), aerosol size distribution, along with other physical, chemical, and meteorological parameters, were measured in six intensive experimental periods of about one day each. The experimental data and analysis are reported in Aerosol Measurements in Los Angeles Smog (1971) and by Whitby et al. (1972a, 1972b), Husar et al. (1972), Ensor et al. (1972), Thielke et al. (1972) and Miller et al. (1972).

A second major photochemical aerosol characterization study is now in progress. The study, aimed at the Los Angeles aerosol, is sponsored by the State of California Air Resources Board and is being conducted by North American Rockwell with the participation of a number of universities and laboratories.

Viewed from the standpoint of air pollution control, the objective of aerosol measurements is to relate both gaseous and particulate source emissions to urban aerosols which are responsible for visibility impairment and possible health effects. The goal, then, is to account in as much detail as possible for the origin, atmospheric concentration, and fate of atmospheric particles. Knowledge of the following elements are required to achieve this goal:

1. Aerosol sources: automobile and industrial emissions, natural aerosol production, etc.
2. Meteorological parameters: inversion height, wind speed and direction, relative humidity, temperature, solar radiation intensity, etc.
3. Chemical and physical rate processes: gas-gas reactions, gas-particle reactions, nucleation, condensation, coagulation, growth by absorption, adsorption, etc.
4. Removal mechanisms: settling, washout, etc.

At this time the full modeling of combined gas and particle behavior in an urban atmosphere is beyond our capabilities.

This is primarily due to our lack of understanding of aerosol sources, growth kinetics, and interactions with the gas phase constituents. The principal focus of an experimental program, then, is to obtain the data necessary to understand these aspects and eventually enable mathematical modeling of urban aerosol dynamics.

We consider first the question of an aerosol "source inventory" for an urban area. The compilation of an aerosol source inventory is more difficult than the compilation of a gaseous emission inventory because:

1. Primary sources can be either anthropogenic or natural.
2. Of the aerosols of anthropogenic origin, a significant quantity are formed in the atmosphere (secondary) and cannot be accounted for in a primary emissions inventory.
3. Aerosols are distributed not only with respect to chemical composition but also with respect to size.

Hidy and Friedlander (1970) have estimated the relative importance of major natural and anthropogenic sources of the Los Angeles aerosol from limited data on their chemical composition. The fractional contribution of each source was estimated from data on emissions of gases and particles, in combination with the use of tracer elements from some sources. Their results suggest that about two-thirds of the Los Angeles aerosol is anthropogenic. Of this, as much as one-third is secondary in origin, coming from chemical reactions or condensation of vapors in the atmosphere.

In subsequent studies, Friedlander and his colleagues (Miller et al, 1972, Friedlander, 1972) have developed a novel means for estimating the contribution of various sources to the atmospheric aerosol measured at any point in an airshed. The method is essentially based on a mass balance for various individual elements which are known to come primarily from certain well-defined sources such as:

Sodium - sea salt
Aluminum - soil dust
Lead - automobile exhaust
Vanadium - fuel oil flyash

Using the data from the 1969 Pasadena Smog Experiment, Friedlander estimated that 15% of the particulate matter resulted from primary natural sources and 25% from primary anthropogenic sources. About a third of the total was estimated to result from atmospheric reactions. About 70% of the total particulate burden was accounted for, with water probably making up a significant portion of the remaining 30%.

It is important to stress that an ordinary source inventory based merely on estimates of emission rates from various sources is inadequate for aerosols because it is uncertain how much material is emitted from sources such as the soil and the sea. In addition, the fraction which remains airborne is often unknown. The mass balance method circumvents these difficulties by essentially employing certain characteristic elements, such as the four listed above, as fingerprints for specific types of sources. In some cases, particularly for the elements carbon, sulfur, and nitrogen, it is necessary to have some information on the combined state in order to know whether an element is present in the gas or particulate phase. In the first two studies (Miller et al. 1972, Friedlander, 1972) the chemical composition has been averaged over the size spectrum. A recent study (Heisler et al. 1972) included the effect of a size distribution. From the contributions of the separate sources and measured size distributions and chemical compositions from the literature, Heisler et al. estimated the size and chemical element distributions of the atmospheric aerosol.

The second area requiring study involves formation mechanisms and rates of particle growth. The two basic questions of interest are (Husar and Whitby, 1972):

1. What is the primary mode of gas to particle conversion: homogeneous or heterogeneous nucleation?*

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* In *homogeneous* nucleation particles are formed in the vapor phase by molecular clustering without the aid or intervention of foreign nuclei. In *heterogeneous* nucleation foreign particles are present in the vapor and act as nuclei for the growing particles.

2. Is the particle growth rate controlled by a surface catalyzed reaction which proceeds at the particle-gas interface, or is the diffusion rate of the vapor phase toward the particle surface the rate-controlling step?

Husar and Whitby have attempted to answer these questions in a series of laboratory studies, the results and conclusions of which are summarized in Chapter IV.B.1. However, much remains to be done. In particular, in order to meet the objectives of understanding the formation, growth, and removal mechanisms of photochemical aerosols, attention must be given to the following needs:

1. *Development of analytical apparatus for measuring aerosol composition.* The development of a source inventory will depend on the accurate measurement of the elemental composition of the aerosol. There is a need for an instrument capable of continuous, real-time measurements of the key inorganic components of particulate matter, including Pb, Na, V, Zn and Ba. There is no commercially-proven device currently available for the continuous monitoring of the elemental components of particulate matter, although X-ray fluorescence techniques are promising (Friedlander, 1972). For example, neutron activation analysis sensitivites for V and Pb are approximately 0.002 and 0.5 micrograms, respectively, corresponding to the total particulate matter in about 100 liters of Los Angeles air.

To obtain enough aerosol for a measurement, air must be withdrawn over a period, leading to a time-averaged reading.

2. *Knowledge of the conversion rates from gas to particles for key species such as carbon, sulfur, and nitrogen.* Most of the carbon-containing compounds in photochemical smog are present in the gas phase. The carbon-containing portion of the aerosol, however, represents a significant fraction of the particulate phase, about 20% in reported measurements (Miller et al. 1972). With associated hydrogen, oxygen, and nitrogen, the organic constituents represent a major portion of photochemical aerosol on a weight basis. Details of the hydrocarbon conversion processes from gas to particle phase are not well understood. It has been found that cyclic olefins are particularly susceptible to aerosol formation in photo-oxidation systems. The opening of the ring and formation of polar groups, such as the carboxylic acid group, lead to non-volatile products. (Glutaric acid has a melting point of 97.5°C, while the corresponding cyclic olefin, cyclopentene, has a boiling point of 44°C.) Several possible mechanisms may control the conversion of carbon from gas to particulate phase: (a) reaction in the gas phase, followed by homogeneous nucleation, (b) condensation on foreign nuclei, and (c) diffusion to existing

particles, followed by surface reaction.

A very important need is the development of an accurate means for measuring the concentration of not just total carbon, but of individual organic compounds in the aerosol. The complexity of current wet-chemical methods is evident in the recent study of Cukor et al. (1972), who measured organic fractions in New York City aerosol. Gas chromatography and mass spectrometry offer promise in this regard. Sulfates in aerosols result from:

a. Photochemical oxidation of $SO_2$ in the gas phase, followed by condensation

b. Oxidation of $SO_2$ in liquid drops with metal ions, and

c. Catalytic oxidation of $SO_2$ on solid particles.

Nitrate formation results from:

a. Reaction between $NO_2$ and NaCl and

b. Photochemical oxidation followed by condensation.

Determination of the particular types of sulfate and nitrate compounds formed is needed.

3. *Ability to reconstruct the measured atmospheric spectrum of aerosol properties, notably with respect to size and chemical composition, given the characteristics of the known sources and conversion mechanisms.* This will require accurate measurement of:

   a. Size distribution for particles of diameter $\geq 0.01\mu$

   b. Chemical composition as a function of particle size

   c. Total particle mass concentration

   d. Total number concentration.

   "At present it is possible to collect data on a routine basis for (a) the size distribution of atmospheric aerosols in the range above $0.2\mu$ in diameter, and (b) the chemical element compositions for many species integrated over all sizes. For research purposes it is possible to measure size spectra for particles larger than $0.01\mu$ and to fractionate chemical element composition rather coarsely with respect to particle size" (Heisler et al. 1972).

4. *Understanding of the fate of elements, such as Pb, Zn, V, Ba.* It is not known what fraction of the total mass of these elements that is found in the atmosphere leaves an airshed to be removed ultimately by washout, and what fraction is actually deposited within the

airshed as a result of various scavenging and removal processes.

A measurement program should be planned so as to meet as many of the stated objectives as possible. Therefore, at each measuring station, it is recommended that the following measurements be made:

- Size distribution of particles $\geq 0.01\mu$
- Chemical composition as a function of particle size
  - Elemental (Pb, Na, V, Zn, Al, etc.)
  - Organic compounds
- Gas phase concentrations (NO, $NO_2$, $O_3$, $SO_2$)
- Relative humidity and temperature
- Total mass concentration
- Total number concentration.

Since these measurements will necessarily involve expensive equipment, they can only be made at a few selected locations at the same time. A feasible program, therefore, is to measure the properties listed at two (or more) points along a common air trajectory. The data analysis could include consideration of sources between the two points and atmospheric conversion mechanisms occurring during the aging and traversal of the aerosol. Such a procedure is currently being employed in the California Air Resources Board aerosol characterization study.

It should be emphasized, in closing, that the main purpose of the atmospheric study of aerosols is their characterization. More ambitious goals would appear to be illusory, as the phenomena of interest are extremely complex and the atmosphere is a poor laboratory. Rather, if characterization can be successfully accomplished with respect to both physical and chemical parameters, *and* if we can devise suitable means for generating aerosols having the same properties as those found in the atmosphere, then the chamber will be the proper laboratory for the study of aerosols.

### 2. Surface Sinks

In Chapter V (pp. 248-251) we reviewed the laboratory and outdoor canopy studies that have been carried out to investigate the nature of surface scavenging processes. We also recommended experimental studies that may be pursued in a controlled environment which might shed further light on the dynamics of surface removal mechanisms. In this section, we consider, as a natural extension of the earlier discussion, observation programs that might provide further information of value.

As very little has been done to date to formulate a basis for estimating losses to surface sinks, establishment of relatively simple correlations should prove to be an important step forward. We thus view data collection with regard to surface sinks at two levels of effort--one quite unsophisticated, the second with some degree of concern for the effects of various parameters on adsorption rates. The decision to mount either effort, however, must await the results of chamber studies recommended in Chapter V. These must indicate that specific adsorption rates are sufficiently high that vegetation can and does constitute an important sink. In order to arrive at simple correlational relationships, we recommend that a survey of unpaved land area be carried out in order to estimate surface area per unit land area of different classes of vegetation and of soil. This should be carried out on a subdivided grid, so that spatial distribution of sink materials is accounted for. Assuming that pollutant concentrations and wind parameters will be measured in any case, and that specific adsorption rates have been estimated as a function of temperature, humidity, and radiation intensity for different pollutants, we will then have a basis for estimating the total mass adsorption per unit time. The estimate would, of course, be crude, within a factor of two or three, assuming that aerosol uptake rates are known to within ± 50 to 100% at the time.

In order to try to estimate the effects of transport on loss rate to surface sinks, surface roughness and turbulence intensity levels must also be determined, preferably taking into account spatial variations. Lettau (1970) has summarized means for estimating surface roughness. Turbulent intensity can be measured as suggested in Chapter III. However, to properly treat this aspect of surface adsorption, a turbulence model for the surface layer is needed.

A more rigorous approach to the treatment of surface sinks may be provided by the mathematical modeling of pollutant removal mechanisms, the equation for the conservation of mass serving as the basic relationship. For conditions of high pollutant concentrations, the dominant terms in the equation will be the time-dependent term and the diffusive and chemical reaction terms. The rate of absorption at the surface will enter as a boundary condition. Successful implementation of this approach will yield analytic relationships between the various physical parameters, such as the diffusion coefficient, the gas phase reaction rate, the surface properties, etc. However, before such rigorous modeling can be meaningfully undertaken, a great deal more must be learned about surface absorption, hence the need for both the chamber and field studies recommended in this report.

## C. Spatial and Temporal Variations in Solar Radiation

Solar radiation in the lower atmosphere both initiates and sustains the photochemical reaction process. In particular, the photolysis of nitrogen dioxide and nitrous acid are initiated by absorption of radiation in the ultraviolet region of the solar spectrum. In Chapter V, we discussed the importance of simulating the intensity, as well as spectral distribution, of irradiation in smog chamber experiments. The eventual goal is to establish a firm relationship between the rates of photolytic dissociation reactions and the intensity of radiation with given spectral composition. Unfortunately, the relationships obtained from chamber tests alone are not sufficient for either modeling the photochemical reaction processes in an urban airshed or interpreting the data collected in an atmospheric experiment involving chemical reactions. Chamber results must be augmented by tropospheric measurements of the radiation intensity and its spectral composition. Such observations are necessary because it is unlikely that radiative transfer processes will be amenable to theoretical description in the near future. We note, however, that present techniques for measuring solar radiation are subject to some controversy, as will become apparent in the subsequent discussion.

In this section, it is our purpose to suggest the need for measurements of solar radiation that are of considerably broader scope than are normally carried out. We envision three objectives in mounting this effort:

> To provide information needed in atmospheric modeling studies and in the refinement of models

To provide a basis for establishing correlations between radiation intensity both at the earth's surface and aloft as a function of the size distribution and concentration of aerosols (haze) and of cloud cover.

To provide data for other air pollution studies, such as fundamental studies in atmospheric chemistry, correlation studies to establish oxidant levels as a function of various parameters, and the like.

We first present a discussion of the spatial and temporal variability of solar radiation intensity in the lower troposphere. We then briefly discuss various techniques for measuring ultraviolet radiation. We conclude with recommendations for an observational program.

Solar radiation entering the uppermost layers of the planetary atmosphere can essentially be considered to be black body radiation at about 6000°K. Only minor variations from this distribution, consisting of many absorption lines (the Fraunhofer lines) of the component elements of the solar atmosphere (hydrogen, sodium, etc.), are present in the solar spectrum. As the solar radiation reaches the stratosphere, most of the electromagnetic energy below 3000 Å is absorbed by ozone, which has a peak concentration at an altitude of about 25 km. The irregularities appearing in the solar spectrum at the earth's surface are caused by the absorption and scattering of the radiation by natural constituents in the atmosphere and by man-made air pollutants in the lower troposphere. The causes of these irregularities may be conveniently classified as the following:

1. Rayleigh scattering due to the gaseous components of a clean atmosphere (i.e., blue sky scattering).
2. Absorption due to the gaseous components of a clean atmosphere (notably water vapor and carbon dioxide.
3. Scattering and absorption by water droplets (clouds).
4. Scattering and absorption due to aerosols.
5. Absorption due to man-made gaseous pollutants (notably nitrogen dioxide and nitrous acid).

As the first two effects occur in clean as well as in polluted atmospheres, as they are virtually invariant with location and time, and as they are in any event relatively well understood, we will be concerned here only with the last three types of effects.

The *temporal variation* of the solar radiation, as affected by the solar zenith angle, is well known. At a particular location on the earth's surface, the solar zenith angle depends upon the:

1. Latitude of the location
2. Time of the day
3. Day of the year

The solar zenith angle for any locality can be obtained from accurate astronomical calculations.

Although the change with solar zenith angle is primarily responsible for the temporal variation of solar radiation, significant variations in intensity and in spectral content is also caused by the diurnal appearance of haze in the urban atmosphere. While solar radiation can accelerate the formation of smog, gaseous contaminants and aerosols can also alter the incoming or outgoing radiation by absorption and scattering. Measurements made by Scott Research Laboratories at Commerce and El Monte in 1969 have clearly demonstrated the effect. Deviations of the observed intensity-time relationship from a near parabola, as expected from solar zenith angle change, ranged from 20% to more than 50% during mid-day or afternoon, when smog formation is intense. Supportive of these observations, Randerson (1970) has reported a 23% loss in the radiation intensity due to the presence of atmospheric pollutants.

As we have stated earlier, cloud cover, aerosol content, and gaseous pollutant concentrations can greatly change with the intensity and the spectral distribution of the incoming solar radiation. Since these variables may be expected to exhibit spatial variations, solar radiation intensity, as experienced by an air mass in the atmosphere, may similarly be expected to vary from place to place. Bach (1971) has studied the *vertical attenuation* of solar radiation over an urban area. He found that the extinction due to air molecules is dominant in the higher and relatively cleaner portions of the atmosphere. Within the shallow layer of the atmosphere directly above the ground (about 50 meters thick), however, anthropogenic pollutants, particularly aerosols, are primarily responsible for radiation attenuation. In particular, Bach observed a difference of 35% in total solar attenuation between "clean" and "polluted" atmospheres.

*Horizontal variations* are more difficult to characterize. Idso (1972) has recently published solar radiation measurements made in metropolitan Phoenix area over a period of several years. The results, in terms of both long-term trends and diurnal variations, are considered in light of concurrent meteorological conditions, as well as with regard to the spatial and temporal variations of airborne particulates.

Difficulties in characterizing solar radiation in an urban airshed have compelled the investigator to resort to real-time measurements. Hopefully, continuous radiation data, collected at a sufficient number of locations in an airshed, will, through extrapolation, provide a complete picture of the temporal and spatial distribution of radiation within the airshed.

In the past, there have been a number of techniques used to measure ultraviolet radiation. Among them are:

1. Filter-Photocell sensor (Eppley sensor).
2. Filter-Phototube sensor.
3. Photochromic glass sensor.
4. Photosensitive plastic sensor.
5. Photochemically-treated filter paper.
6. Photochemical reaction cell.

The most widely used are the filter-photocell sensors for general UV measurements and the photochemical reaction cell for air pollution studies. The latter technique, first proposed by Tuesday (1961), permits the determination of radiation intensity by observing the apparent decomposition rate of nitrogen dioxide. As discussed in Chapter V, the photochemical reaction cell can be used to measure $k_1$ accurately and quickly.

From the preceding discussion it is clear that radiation intensity not only varies with ground location (x, y), elevation (z), and time (t), but that its variation with x, y, z, and t is, or can be, sufficiently strong that it must be accounted for if accurate modeling of the atmosphere is desired. As a result we recommend that, as a part of a comprehensive monitoring program, radiation intensity be measured at a number of locations throughout the urban area, that it be measured as a function of time, and that it be measured on an airborne platform above the ground monitoring sites (aircraft, helicopter, etc.) as frequently as the monitoring program permits. While it may not be possible to make airborne measurements on a routine basis, they should be made with sufficient frequency that a variety of aerosol size distributions and concentrations and levels of cloud cover are concurrently observed. It is, of course, essential that the physical properties of the atmospheric aerosol are properly characterized if correlational relationships are to be derived. To this end, we recommend that the size distribution and the concentration of the aerosol be measured in conjunction with solar intensity observations. (See Whitby et al. (1972) for a discussion of measurement procedures.)

## D. Measurement and Identification of Chemical Species

Concern has been expressed from time to time that chemical mechanisms, when applied in the simulation of atmospheric reactions, are oversimplified. While this claim is clearly a valid one, it should be pointed out that the simplified structure of currently used mechanisms is a reflection of

> Our level of understanding of the important reactions contributing to atmospheric photooxidation processes

and

> The limited number of species for which concentration-time profiles are available.

The application of more detailed mechanisms in atmospheric modeling is justifiable only if they can be validated; thus, a broader and more complete data base, in terms of number and type of species monitored, is presently needed. In this section, we consider, albeit briefly, both the monitoring and the identification of pollutant species in the atmosphere.

At the present time four *individual* chemical species and two *classes* of species that are found in the atmosphere are monitored on a routine basis--NO, $NO_2$, $SO_2$, CO, hydrocarbons and oxidants. Measurements of the two classes of species are of little value from the viewpoint of developing and applying chemical mechanisms. In particular, total carbon analysis does not reflect the "reactivity" of the atmospheric hydrocarbon mix, and ozone, not total oxidants, is the species included in all photochemical kinetics mechanisms. We thus recommend that

> More detailed analysis of hydrocarbons becomes a routine feature of atmospheric monitoring. At present it would be useful to measure the concentrations of the following groupings*:

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* Unfortunately, no simple technique has yet been devised to measure these groupings in the atmosphere. Infrared analysis, however, does hold some promise in this regard. For instance, terminal olefins absorb at frequencies between 905-910 $cm^{-1}$, aromatics (including benzene) at frequencies of 690 and 760 $cm^{-1}$, and aldehydes, acids, and ketones in the region of about 1735 $cm^{-1}$. Until techniques for infrared analysis become sufficiently well refined, however, more complete measurements of the hydrocarbon mix using computerized gas chromatographic methods must

$C_4^+$ paraffins

olefins, excluding ethylene

aromatics, excluding benzene

aldehydes

ethylene

Ozone be monitored on a routine basis.

In Chapter V we discussed the need for measuring aldehydes, peroxides, and peroxyacetylnitrate (PAN) in smog chambers, both as an aid in model validation and to provide important information concerning the smog formation process. Aldehydes are major products of the oxidation of hydrocarbons, being found in the atmosphere at concentrations of the order of 10 to 20 pphm. Peroxides have been identified as intermediates in the smog formation process and have been measured at concentrations of up to 18 pphm (Bufalini et al., 1972). PAN, also a product of atmospheric reactions, additionally serves as a scavenger for free radicals and $NO_2$, and consequently affects the late time behavior of the chemical dynamics. Because of the important role that each of these species (or class of species) plays, we believe that it would be highly desirable if each were measured on a regular basis in the

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be performed. Unfortunately, as the individual species concentrations are then grouped together, a great deal of information is discarded. (The relative concentrations of the individual hydrocarbons which comprise these groupings change not only from day to day, but continuously throughout the course of the day. Therefore, it does not appear possible to characterize the "reactivity" of the atmosphere by the measurement of three or four key species such as hexane, propylene, toluene, and formaldehyde.)

atmosphere. Unfortunately, monitoring techniques for these species are very poor. Aldehydes and peroxides require wet chemical methods, while measurement of PAN involves long path infrared spectrometry, a procedure not suitable for routine measurement outdoors. Thus, measurement of these species presupposes the development of appropriate analytical procedures.

We believe that it would be worthwhile to attempt to identify two additional species that are believed to be important participants (or products) in atmospheric reactions--nitric and nitrous acid. The roles that these species play in the chemical dynamics have been discussed in Chapters II and IV. If these species are found in significant amounts in the atmosphere, it will be necessary to develop analytical instrumentation that will permit their monitoring on a routine basis.

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